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ABSTRACT

This project considered the feasibility of using an acid flux containing sodium chloride and potassium persulphate for the decomposition of pyrochlore, chalcopyrite and ilmenite concentrates. A procedure involving the flux decomposition of pyrochlore followed by dissolution of the cooled melt in a weak oxalic acid solution appeared the most promising scheme from the point of view that present day techniques require the use of highly corrosive acids and specialized containers for their confinement. Though the fusion procedures offer unique alternatives, the cost of the potassium persulphate component is currently prohibitive, thus making the three proposed processes uneconomic under present conditions.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
CHARACTERIZATION OF THE PURE FLUX	9
Phase Diagram	
Identity of Gases Evolved from Pure Flux	
Identity of the Final Products of Cooled Solid	
Summary	
CHALCOPYRITE	13
Solubility of Chalcopyrite in the Flux	
The Effect of Temperature and Time on Solubility	
Optimum Leach Condition Experiment	
ILMENITE	15
Solubility of Ilmenite in Flux Components	
The Effect of Temperature and Time on Solubility	
Optimum Leach Condition Experiment	
PYROCHLORE	17
Solubility of Pyrochlore in the Flux Compositions	
Time Temperature Solubility Experiments	
Optimum Leach Methods for the Solubilization of Flux/Pyrochlore Solid	
a) Precipitation of Niobium Oxide by Leaching with Water	
b) Solubilization of Pyrochlore/Flux Fusion Product with Oxalic Acid	
Aqueous Leaching of Pyrochlore/Flux Solids	
Decanting Experiment	
Use of Sodium Persulphate in Substitution for Potassium Persulphate	
COST EVALUATION (HATCH ASSOCIATES)	23
SUMMARY	27
REFERENCES	28
FIGURES AND TABLES	31
APPENDICES	
Appendix I — Calculations, Pure Flux Components	
Appendix II — X-ray Diffraction Results (Royal Ontario Museum Report)	
Appendix III — Analytical Data (Energy, Mines and Resources Reports)	
Appendix IV — Analytical Data (X-Ray Assay Laboratory Reports)	
Appendix V — Calculations of Oxalic Acid Uptake	
Appendix VI — Disposal of Spent Solutions (Hatch Associates Report)	

INTRODUCTION

Decomposition, the breakdown of a material into its component parts, is an important step in many chemical procedures. The applications of decomposition procedures may range from the analytical determination of elements in gram-sized samples to the economic extraction of metals or compounds from large tonnages of ore materials. The composition of the starting materials may be homogenous or, more often, heterogeneous. The species of interest may be distributed uniformly throughout the sample or may form a component in a minor phase which itself may represent only a small fraction of the starting material.

Decompositions of geological materials on an analytical scale are usually carried out by some form of acid attack, with either single acids or more commonly mixtures of acids. The attack is usually considered to be partial. A total digestion of the more resistant minerals requires mixed strong acids that include hydrofluoric acid. The reaction sometimes is carried out in a sealed container, a 'bomb', a elevated temperatures.

A number of metals and their compounds that are more or less resistant to attack by acidic or alkaline aqueous solutions can be dissolved by fusion techniques. These techniques take various forms but, in general, the material to be decomposed is mixed with a suitable salt or mixtures of salts which melt at an elevated temperature to form a corrosive, non-aqueous solution. After the reaction has taken place and the melt has cooled, it can usually be dissolved in an aqueous solution.

Chemistry of Flux Decompositions

The most soluble form of many metals is the simple cation in acidic solution. Dissolved species of these metals in more basic solution may eventually hydrolyze and precipitate as oxides or hydroxides. Conversely, the more soluble species of a separate, smaller group of elements may be an anionic entity, e.g. the tungstate ion, WO_4^{--}, which is only stable in a basic solution. Acid digestion is commonly used for the first group of metals whereas some form of base decomposition is needed for the second.

The metal itself represents the reduced form of a metallic element, the cation being its oxidized equivalent. The conversion from the metal to cation thus requires oxidizing conditions. Similarly, metals that normally exist as a cation of low oxidation state may have to be oxidized to a higher state to render them soluble. Copper in rocks, for instance, usually exists as Cu^{+} but can only be solubilized as Cu^{2+}. Solubilization can sometimes be achieved without change of oxidation state by alteration of the pH of the solution as in the conversion of Fe_2O_3 to Fe^{3+} by acidification.

The action of the various flux compositions may be visualized in terms of Eh-pH diagrams for the element or compound to be solubilized. Such diagrams, (e.g. Pourbaix, 1966) outline the stability fields of aqueous species as a function of the oxidation potential and the pH of the solution. These diagrams can only be used as guides to reactions at higher temperatures in non-aqueous systems, but are useful in the evaluation of a particular route.

The fluxes in common use reflect the considerations outlined above. Sodium peroxide, Na_2O_2, for example is a strongly oxidizing, alkaline flux melting at 495°C that can be used for the decomposition of ores of titanium, chromium and tungsten. Its major drawback is the lack of materials or crucibles that are resistant to Na_2O_2 melts at high temperatures.

The alkaline metal carbonate and hydroxide fluxes provide decomposition routes that do not involve change of oxidation state. A eutectic carbonate flux $Na_2CO_3.K_2CO_3$ with a melting point of 712°C has been widely used in the digestion of insoluble or sparingly soluble phosphates, sulphate, fluorides and tungstates. After leaching the melt with water, the anions are brought into solution as their alkali metal salts. Alkali metal hydroxide-carbonate mixtures have also been used for similar applications but require considerably lower temperatures. The major disadvantages with these fluxes is the solubilization of large amounts of silica if present in the sample or container. The silica precipitates as a gel if any subsequent steps in the procedure require acidification.

A mixture of calcium carbonate and ammonium chloride is used as a method for the decomposition of silicates in the determination of alkali metals. The ammonium chloride dissociates to NH_3+HCl. The latter reacts with the calcium carbonate to form calcium chloride. Subsequently, the remaining carbonate releases CO_2 and a mixture of CaO and $CaCl_2$ reacts with the sample to produce calcium silicate and alkaline metal chlorides. The method, which is non-oxidizing, is useful only for the alkali metals.

The persulphate ion, $S_2O_8^{2-}$, is one of the strongest oxidizers known (E_0=-2.01 V). Direct oxidization by persulphate in aqueous solution proceeds slowly but becomes rapid in the presence of catalysts such as the Ag(I) ion. As a molten salt, it has been used to decompose ilmenite (Elbieh and Gabra, 1963). Boron is also dissolved with the liberation of sulphur dioxide (Eberle and Lerner, 1961). Bock (1970, page 256) wrote that persulphate should, in fact, be considered as a disulphate fusion as the melt begins to lose oxygen even at 200°C. Disulphate (often called pyrosulphate) has been widely recommended in the literature for many types of oxide fusions but it is dubious that quantitative recoveries can always be made. Tin was reported (Fairchild, 1943) to be recovered quantitatively as insoluble SnO_2.aq following fusion with $Na_2S_2O_7$ and boiling the solidified melt with dilute nitric acid. From work in this laboratory, quantitative recoveries of tin cannot be achieved using pyrosulphate. Persulphate, contrary to the opinion expressed by Bock, appears to be a much more aggressive oxidizer than pyrosulphate, the critical reactions possibly occurring during the period that oxygen is being evolved. It has been noted that molten persulphate alone evolves very little gas even at 500-600°C. The vigorous evolution of gas only occurs when mixed with a sample undergoing oxidation. It is likely that this reagent, which for equivalent grades is much less expensive than pyrosulphate, is unwarrantedly neglected in the literature.

Scintrex Fluxes

The fluxes developed by Scintrex Limited combine a strong oxidizing agent (e.g. potassium persulphate) with a halide component (e.g. sodium chloride) to form an acid flux. A ternary variant of the flux is formed by the further addition of sodium carbonate to allow more basic conditions to be maintained.

The presence of the chloride is critical to the performance of the flux although its effect seems to vary from acid flux to base flux and between different reactions. In some cases the chloride is required for the actual dissolution in the melt, in others the chloride component may actually lower the solubility of the sample material in the melt but subsequently render the cooled mass more readily soluble in aqueous solution.

The Scintrex fluxes have successfully been used for the solubilization of many metals and geological materials, which are not readily attacked by acid digestions. For example, gold is insoluble in simple acids and can only be put into solution by strong mixed acids. Gold is readily taken up by the flux but is unattacked by persulphate alone. Another example is ilmenite which is solubilized under strongly acid, high temperature conditions. The acid flux reacts with the ore at relatively low temperatures (500°C-600°C) and is easily stored and heated in glass reaction vessels (on a laboratory scale).

A basic flux composition has been primarily tested in the dissolution of the oxyanions of tungsten and molybdenum, the naturally occurring tungstates and molybdates. The flux, for example, will take up some 30% scheelite (by weight) before precipitation of a calcium salt. The solubility of tungsten oxide (WO_3) is, however, at least some 300% by weight so that we can expect that the uptake of scheelite will exceed the 30% figure given above, limited only by the practical considerations of working with a 2-phase melt.

Fluxes are infrequently used as methods of decomposition of ores. A variety of flux components are very commonly added to the ore feed in many pyrometallurgical processes to, for instance, reduce the temperatures required or to form a slag that is fusible and more readily separated from the matte. Beryllium is, however, recovered from beryl using a flux composed of sodium silicofluoride, sodium carbonate and sodium iron fluoride at 750°C (Copaux-Kawecki process). The aqueous solution after leaching contains sodium beryllium fluoride.

The fluxes described are the result of work done in providing quantitative recoveries of certain metals present at ppm or at most low percentage levels in a wide range of geological sample material. Subsequently, when it became clear that there could be metallurgical applications for these fluxes, the same mixtures were tested semi-quantitatively on various ore minerals, ore concentrates and synthetic compounds. Later it was realized that the sulphate alone had significant corrosive potential and studies comparing persulphate to persulphate-chloride mixtures were initiated.

Decomposition of Ore Minerals

Processing of ore minerals on an industrial scale usually starts with some form of beneficiation. Barren or nearly barren material is separated from the more valuable components by use of differences in physical properties, e.g. specific gravity, magnetic properties, etc. The subsequent chemical decomposition of the concentrate is commonly carried out at high temperatures. Smelting and converting processes involve solid-solid or solid-gas reactions to produce intermediate compounds such as metal-sulphide mattes or impure metals which can then be further refined. Hydrometallurgical leaching of ore concentrates is less common but finds important applications in treating specific ores such as in the extraction of uranium.

The fluxes considered in this project were the persulphate to persulphate-chloride mixtures and the mineral ores considered were ilmenite, chalcopyrite and pyrochlore.

Chalcopyrite

Deposits of copper are widely distributed in many geological settings in North America (Canada, United States), South America, Africa, Australia, Europe and Russia (CMY, 1979).

The copper content of a given ore deposit may run from less than 1% to a rich deposit grading 2½ to 4% copper. Chalcopyrite ($CuFeS_2$) assaying approximately 34.6% copper is the most widespread copper mineral and is one of the most important sources of that mineral. Copper tends to associate with other metal sulphide groups (e.g. nickel, zinc, silver, gold). Deposits of copper sulphide most often contain large amounts of gangue minerals and must necessarily be upgraded prior to processing. The type of ore determines the choice of extraction process. Lean ores containing soluble compounds are treated by hydrometallurgy. However, the vast majority of copper ores are sulphide containing and rely, at present, on pyrometallurgical techniques for their decomposition (West, 1982; CMY, 1972).

Few copper ores are suitable for direct reduction and thus beneficiation is essential. The sulphide ore must initially be crushed and ground. Using the finely ground ore and selected frothing agents, a concentrate is produced by flotation which involves separating the sulphide particles from the body of the crushed ore and gangue minerals. The concentrate is then roasted in an oxidizing atmosphere at 500-750°C to reduce the sulphur content followed by smelting with a flux to produce a copper "matte" and slag. The matte typically contains 25%-45% copper, 44-21% iron and 23-25% sulphur. The molten slag which is decanted off principally contains the gangue minerals (silica, ferrous oxide, lime, alumina, magnesia) and less than 0.5% copper. The successful operation of a reverberatory smelter in obtaining a slag which is both fluid and low in copper depends on skill and experience. Upon separation of the matte and slag, the matte is converted to blister copper by oxidation of the iron and sulphur; silica is added to slag off the iron as it is oxidized. The process must be kept at high temperatures (1200°C) in order that magnetite (Fe_3O_4) does not form, since the magnetite makes the slag too viscous and results in excessive copper loss. This blister copper is cast into cakes and subsequently refined into a marketable product (West, 1982).

When considering a new process for decomposition of sulphide ores, operations will, in the future, have to meet certain criteria of cost effectiveness and acceptance by regulatory agencies. Some of the concerns are environmental (both gaseous and/or solid-liquid effluent disposal), energy consumption and amenability to processing "dirty" concentrates.

Various hydrometallurgical processes for the decomposition of copper ores have been researched in the past (Habashi and Yostos, 1977; and Rath et al, 1981) which claim to resolve the gaseous effluent problems, but the literature suggests that these hydrometallurgical routes often create solid/liquid effluent problems, consume large amounts of energy which cannot be compensated for by production outputs, and are not amenable to "retrofit" applications (Herbert, 1974; Traulsen, 1982; Peacey, 1982).

Traditional reverberatory processes have now been outdated due to their high energy requirements, labour requirements and stricter environmental requirements. Oxygen enrichment and oxy-fuel burner technologies are used in the upgrading of the older processes. An oxygen smelting system has also been investigated whereby the exhausted SO_2 is recycled, resulting in an overall decrease in the volume of gas generated during smelting (Yazawa and Tozawa, 1983).

Newer processes which are commonly discussed in the literature include flash smelting (Inco, Copper Cliff smelter, Outokumpu smelter in Ashiv, Japan), Noranda smelting (Noranda Mines) and Mitsubishi smelting (Naoshima, Japan). The flash smelting operations utilize a single burner blast for oxygen/low fuel feeds and the sulphide concentrates become self-combustible (autogenous). A matte is produced containing very low sulphur and 50% to 60% copper. In the Noranda-type smelter the pelletized concentrate (containing up to 10% moisture) is mixed with coal and silica to produce a high grade matte rather than the blister copper. Oxygen enrichment is used in this type of process to reduce fuel requirements. This process is limited to the batch-type operation since it cannot produce a blister copper from relatively "dirty" concentrates. The Mitsubishi process is a semi-continuous process where three furnaces are interconnected; the first being a smelter to produce matte and slag, the second is a settler separating the matte and slag, and finally a converter to produce copper blister and slag from the matte. This process requires a complex gas collection system and is more applicable to lower production requirements. Both flash smelting and the Mitsubishi processes require a dry concentrate feed.

The choice of processing treatment in a particular scenario depends on the delivered cost of power and fuel to a specific plant site, concentrate composition, capital investment required and quantity of SO_2 gases which is tolerable technologically (Traulsen, 1982; Weiss, 1983; West, 1982).

In considering an acid flux type of process, the costs inherent in fuel input, capital equipment, material costs and especially environmental control would have to compete with the pyrometallurgical processes already being used today. A "retrofit" type operation with reduced emissions would act as a definite asset in competing with the current processes.

Ilmenite

Ilmenite ($FeOTiO_2$) and rutile (principally TiO_2) are the only commercially important minerals of titanium. The major sand deposits of rutile are in Australia and Sierra Leone; hard rock deposits of ilmenite are more widely distributed and are located in Australia, Canada, United States, USSR and Norway, to name a few. More than 60% of the world's rutile and 80% of the ilmenite is used as a source for titanium dioxide pigment. All titanium metal produced is by way of "chlorination" of titanium minerals (CMY 1973, 1979).

Ilmenite deposits principally occur in unweathered hard rock and contain only 40-60% TiO_2, the remainder being iron (hematite and magnetite), silica, feldspar and gangue minerals. The removal of these contaminants necessitates crushing and grinding of the raw ore, followed by separation of the siliceous gangue by magnetic or gravimetric techniques. The upgraded product is calcined to lower the sulphur content and, finally, smelted to produce a titanium slag and molten iron. This pigment-grade titanium slag contains approximately 70-72% TiO_2. Rutile sand deposits, on the other hand, are easily mined and cleaned of contaminants by gravimetric and magnetic techniques. The result is a much superior concentrate (greater than 90% TiO_2) (CMY, 1973; Dooley, 1975).

The sulphate production of pigment-grade TiO_2 involves digestion of the titanium slag with sulphuric acid. The product is dissolved in water to give a solution of titanyl sulphate together with soluble impurities and unreacted solids in suspension. Following clarification and filtration, crystalline titanium oxide hydrate is precipitated. The precipitate is then calcined and ground. The chloride process uses rutile concentrate or very high grade titanium slag (>85% TiO_2) as the raw material. This raw material is mixed with carbon and chlorinated at high temperature to produce titanium tetrachloride, a volatile colourless liquid. The titanium tetrachloride is then either oxidized to produce titanium dioxide or treated to produce titanium metal sponge. In this process the chlorine is recovered and recycled (CMY, 1973; Judd, 1973 and Bureau of Mines 1970, pp 773-780).

Due to their high content of MgO and CaO (5% and 1% respectively), Canadian slags are used as raw materials in the sulphate process only. These constituents can lead to operational problems in the chlorination process. A high iron content would result in high iron chloride levels and would pose serious disposal problems. The excessive attendant loss of chlorine could also not be economically tolerated. Ilmenite slags, in particular Canadian slags, are therefore treated by sulphation. Natural rutile concentrate, however, because of its high TiO_2 and low impurity level is directly suitable for the chloride process. In the United States, titanium production largely involves rutile processing by chlorination. Most producers favour chlorination over sulphination because of the ease of rutile introduction into the process and also because of the apparent cost and waste management advantages (Dooley, 1975; Rosenbaum, 1983).

Increasing world demands for higher quality titanium slags, and shrinking reserves of rutile, is forcing industry to look at the development of an alternate, more economical process with reduced waste problems and/or to consider the

production of a "synthetic rutile" made from hard rock ilmenite to be used as a feed for the chlorination process. It was the purpose of this program to examine the Scintrex acid flux for application either as a substitute method of processing the ilmenite slag in the production of titanium products, or as a cost effective method of producing synthetic rutile.

Pyrochlore

The principal commercial mineral of niobium is pyrochlore. Pyrochlore deposits are most abundant in Brazil and Canada. A second source of niobium is from the mineral columbite ($(Fe,Mn)O.Nb_2O_5$) which occurs in residual and placer deposits, and is generally recovered as a by-product of tin mining or as a co-product of tantalite-columbite operations. Columbite concentrates are extracted from deposits in Nigeria, Australia, Zaire, Thailand and Mozambique (CMY, 1973, 1979).

Canadian pyrochlore occurs in complexes of carbonate-rich rocks in which the mineral pyrochlore constitutes approximately 0.8-1.9% of the ore (i.e. 0.5% Nb_2O_5). Prior to shipping, the ore is concentrated by physical methods (e.g. wet gravity, electrostatic techniques) resulting in a niobium oxide content of 50-55% with small amounts of rare earths (e.g. cerium) and radioactive elements (e.g. uranium, thorium) (Habashi and Malinsky, 1975).

It is rarely possible to associate one chemical composition for pyrochlore with any one locality. Pyrochlore group minerals have the general formula:

$$A_2B_2O_6F$$

where A is principally Na^+ Ca^{2+} (in some deposits the A positions can be otherwise substituted) and B is Nb^{5+}, Ti^{4+}, Ta^{5+}. Pyrochlore from Quebec deposits is typified as: $CaONb_2O_5NaF$ (Niobec Research Report, 1981).

Niobium ore concentrates have recently been in increasing demand. The steel industry is the largest consumer of niobium, used in the form of ferroniobium as an additive in high strength - low alloy steels, carbon steels, stainless steel, and super alloys (CMY, 1979). Some of the pyrochlore from Quebec is exported. An inexpensive method of producing a concentrate 95% Nb_2O_5 would therefore reduce shipping costs substantially.

There have been many methods proposed in the past for the decomposition of pyrochlore and other niobium-bearing ores. Some methods may be of industrial importance, and others are more applicable to laboratory conditions. These methods vary significantly depending on the niobium ore body tested.

Miller (1959) discusses numerous alkaline and acid fluxes which were tested or have been used as decomposition media for columbite-tantalite minerals. Some methods involved the solubilization of the impurities away from the insoluble niobate or tantalate, such as in the case of the alkaline fluxes: sodium hydroxide, sodium carbonate. Another example of this fusion technique was discussed by Gutison and Cemerazzo (1971) where sodium nitrate was fused with columbite-tantalite concentrate resulting in the formation of insoluble sodium

niobate and tantalate upon leaching with water. The solid mass was subsequently digested in acid solution to remove excess impurities (e.g. iron). The beneficiated product contained 40-50% $(Ta,Nb)_2O_5$ from the tin slag containing 8% $(Ta,Nb)_2O_5$ prior to processing. Other alkaline fluxes which have been evaluated are potassium hydroxide and potassium carbonate where the fusion product is digested with water. Manganese and iron impurities are insoluble and the leach liquor contains the soluble potassium tantalate and niobate together with the titanate, silicate and other impurities.

The acid flux fusions which Miller discusses follow much the same methodology as the alkaline fluxes, and similarily do not involve the decomposition of a pyrochlore concentrate. Materials such as potassium bisulphate, sodium pyrosulphate and potassium hydrogen fluoride are some of the fusion media discussed.

Acid digestion techniques have also been tested for the decomposition of niobium-bearing minerals. Two methods have been suggested for the decomposition of Canadian pyrochlore. The first, chlorination, is discussed by both Miller (1959) and Habashi (1975), whereby the pyrochlore was chlorinated in the presence of SO_2 or carbon, (reducing agent), causing the niobium to volatilize as $NbOCl_3$. The $NbOCl_3$ was then treated to precipitate a 95% Nb_2O_5 product with the rare earth and thorium constituents extracted separately from the chlorination residue by leaching with water. This process has been considered in lab scale experiments only.

The method of acid digestion which is presently employed is the decomposition of pyrochlore with hydrofluoric acid followed by solvent extraction into methyl isobutyl ketone (MIBK). The niobium and tantalum is then back extracted out of the MIBK into a dilute acid solution. Tantalum and niobium are separated with their respective "strip solutions" and precipitated as hydroxides with ammonia. The oxide is obtained after calcination (Borchers P. and Korinek, G.J., 1981).

The major objections to this process are:

a) The consumption of expensive HF acid for the digestion of non-valuable constituents such as the oxides of silicon, titanium and iron.

b) Special materials are required for handling the highly corrosive solutions (e.g. acid resistant containers, filtering devices, etc.).

The purpose of testing the acid flux developed by Scintrex for the decomposition of pyrochlore was to investigate whether the cost of using this flux could reduce present processing costs and at the same time eliminate the present process limitations.

CHARACTERIZATION OF THE PURE FLUX

As a step in designing a fusion process for the decomposition of ilmenite, pyrochlore or chalcopyrite, the physical and chemical properties of the flux itself were studied.

Since the flux is a two component system, a range of compositional variations can be considered; the optimum being the lowest melting, yet least expensive mixture which will yield the greatest solubility of a particular ore in the melt. The first section of this project deals with the pure flux components, the melting point data, gases exhausted and final products. This information coupled with the solubility of each ore in a particular flux composition, the effect of time and temperature of solubilization and optimum process flow incorporating the fusion technique will determine the viability of the Scintrex acid flux for the decomposition of these particular ore concentrates.

Phase Diagram

The two component phase diagram of potassium persulphate and sodium chloride was studied by a method of thermal analysis, whereby heat was withdrawn from a series of molten samples at a steady rate (e.g. cooling curves). The rate at which the system loses heat is a function of the net heat capacity of the system and the rate at which the components dissipate the heat. When a component begins to precipitate, its latent heat of freezing is liberated contributing an overall heat input into the system, thereby slowing the cooling rate of the components. On a cooling curve this phase change is observed as a "break" in the curve. At the end of the break the component has completed precipitation and cooling resumes at the original rate until a second component begins to solidify. Experimental cooling curves may show small temperature minima at breaks and halts, due to supercooling. The location and lengths of the various breaks and halts in the cooling curves are used in plotting the phase diagram.

Samples containing twenty grams of flux, ranging in composition from 0% sodium chloride/100% potassium persulphate to 65% sodium chloride/35% potassium persulphate were prefused in pyrex test tubes prior to the determination of their cooling temperature profiles. Cooling curve profiles were therefore not determined for pure $K_2S_2O_8$/NaCl mixtures, but rather the prefused products from such mixtures. (Gases formed during the initial $K_2S_2O_8$/NaCl reaction were evolved during this prefusing stage). The experimental setup is depicted in Figure 1. The furnace and recorder were calibrated using inorganic compounds with known melting points.

The recorded temperature changes versus the actual temperature changes of the reaction melt will be a function of the sensitivity of the measuring system. The measuring sensitivity is affected by the rate of heat conductivity of the measuring system, the heat capacity of the thermocouple quartz encasement and reaction vessel versus the total increase in the net heat capacity of the reaction of the two components, and the length of the reaction. For example, if the reaction duration is small in comparison to the required time to conduct the

reaction heat through the quartz cover to the thermocouple, then the thermocouple may not detect the reaction which had occurred. Secondly, if the latent heat of the reaction is small in comparison to the heat required to equilibrate the thermocouple measuring system, the recorded temperature profile may not reflect the phase change. Another condition which is crucial when generating the cooling curves is the cooling rate. If the cooling rate is too fast, phase freezing occurs at high temperatures.

The freezing points interpreted from the cooling curve plots are listed in Table 1 and plotted in Figure 2. "$K_2S_2O_8$" refers to the prefused state of the potassium persulphate.

For flux compositions containing 0-18% sodium chloride, the freezing points determined, rendered the interpretation of this region of the diagram complex. A better understanding of the fusion products present, perhaps using x-ray analysis, would verify the true reaction points in this area.

The region 18% to 100% sodium chloride appeared to show a eutectic composition at 25% sodium chloride and a peritectic at 45% sodium chloride. In the region 42 to 50% sodium chloride the curve deviated from the proposed peritectic line. This deviation may have been an artifact related to heat transfer problems and reaction duration. Kinetics may also have played a role in causing this effect, due to instabilities in the melt causing the reaction temperature to drop well below the peritectic before the reaction was triggered.

In order to more closely define the phase relationsips, further work would be required: the temperature measuring sensitivity should be more accurately evaluated and qualitative analysis of compounds formed in the region of 0-18% sodium chloride should be conducted in order to clarify the state of the phase relationships. Further investigations in the region of 42-50% sodium chloride should also be made to determine the cause of the offset phenomenon from the peritectic.

The phase diagram did, however, indicate the complexity of the sodium chloride/potassium persulphate relationship. The lowest melting composition appeared to be 5% sodium chloride/95% potassium persulphate; however, compositions up to 25% sodium chloride/75% potassium persulphate appeared also to be low melting fluxes for the decomposition of the copper, titanium and niobium ores.

Identity of Gases Evolved From a Pure Flux Composition

The mixture of sodium chloride and potassium persulphate, when heated, evolved a highly corrosive gas that appeared to play a vital role in the decomposition of some ores (e.g. gold), but not in others (e.g. copper, iron, zinc). The components of this gas were suspected to be SO_2, SO_3, S, O_2, Cl_2 and an oxychloride gas (e.g. OCl, OCl_2). Spot tests, recommended by Feigl (1972) indicated the presence of oxychloride (or less likely, chlorine) and trace sulfur dioxide.

Samples of flux (50% sodium chloride/50% potassium persulphate) were fused and the gases were collected in various absorbing liquids (specified by the respective ASTM methods). Argon gas was used as a purge gas and to maintain continuous flow of the gas to the collection medium.

Sulphur Gases: ASTM method D2914-78, "Sulphur Dioxide Content of the Atmosphere" (West-Gaeke Method) was used to determine the sulphur oxides in the gas stream. The gas evolved from the 3 gram sample of flux (containing 1.5 grams of potassium persulphate) was found to contain 0.155 mg of SO_2 which was therefore considered to be trace SO_2. If any SO_3 was present, it would not have been indicated by this method.

Oxygen Gases: ASTM Method D888-66 was used to determine the oxygen content in the gas stream. This was a colorimetric method where dissolved oxygen reacted under alkaline conditions with an indigo carmine indicator solution. When the sample was injected with the indicator, no colour was apparent, indicating no oxygen content in the gas stream. This test is sensitive to less than 1 ppm oxygen concentration.

Chloride Gases: A sample of flux weighing 1.0 gram (0.5 grams NaCl/0.5 grams $K_2S_2O_8$) was fused and the evolved gas was collected in 1000 ml pH 10 water which was subsequently analyzed by the Mohr method (Brown, E., et al, 1970). The quantity of chloride present (as Cl^-) was found to be 110 mg which corresponds to 36% of the original sodium chloride evolved as gas. This value was rather high. The level of chloride was determined from the quantity of silver nitrate dispensed in the analysis, and since the silver nitrate could react with the oxidizing components and the chloride present in the test solution, a higher quantity of oxychloride gas may have been indicated than was actually evolved.

The test did serve to demonstrate however, that the primary gas evolved from a flux containing 50% sodium chloride/50% potassium persulphate, by weight, was either a chloride or oxychloride.

Identity of Final Products of the Cooled Solid

When fusing the two component flux (sodium chloride/potassium persulphate) the by-products which potentially could be present were: pyrosulphate (S_2O_7), sulphate (SO_4), persulphate or thiosulphate and chloride or oxychloride. Spot tests (Feigl, 1972) were conducted and determined that no persulphate or oxidizing chloride were present.

Melting point data seemed to indicate that the sulphate was present as pyrosulphate (or a decomposition product of pyrosulphate). To quantify the level of chloride and sulphate (presumed to be as pyrosulphate), therefore, 5 grams of flux (2.5 grams sodium chloride/2.5 grams potassium persulphate) were fused and dissolved in 100 ml deionized water. This solution was then used in the following analytical tests.

Sulphate: ASTM method D516-68, "Sulphate Ion in Water and Wastewater", was used to determine the sulphate content in the solution. The result of the test

showed that 24% of the potassium persulphate in the original sample was not accounted for. This material could have been present as a different reaction product or as undetected SO_3 gas. It should, however, be taken into account that the persulphate was found to contain a considerable amount of moisture, which would have accounted for some of this weight loss. The high concentration of chlorides in the sample may also have interfered with the sulphate test.

Chloride: The quantity of chloride in the test solution was determined by the Mohr method (Brown, E. et al, 1970). From the 2.5 grams of sodium chloride used in making the flux, 2.45 gms NaCl was represented after fusion. Therefore 98% of the original material used was accounted for. The .05 gms of sodium chloride not accounted for in this analysis was considered lost in gas evolution (see calculations, Appendix I). The analysis of the cooled solid appeared to be more reliable than the gas analysis due to the absence of potentially complex oxidizing agents which would probably have interfered with the analysis.

Summary of Results on Pure Flux Components

1. The products of a fused melt of persulphate and sodium chloride are not easily determined, as can be visualized by the phase diagram.

2. The gas evolved during fusion for the 50/50 flux composition was most likely an oxychloride. Trace SO_2 was also observed.

3. Most of the sodium chloride component could be accounted for (98% solid; 2% as gas), however, some 24% of the sulphate component was not accounted for. This discrepancy was believed due to moisture in the original persulphate and chloride interfering with the sulphate test.

After examining the products of the pure flux, each ore was examined for its solubility in the melt. Subsequently, the most aggressive flux mixture for the decomposition of a given ore was sought, and finally the optimum method for leaching the flux/ore solids to obtain a saleable product was determined.

CHALCOPYRITE

The major objection in refining sulphide ores is the evolution of large volumes of sulphur dioxide gas. Environmentally, it would be desirable if a process existed which would circumvent the evolution of this gas. This section will consider the viability of using a flux to decompose chalcopyrite and produce the more desirable by-product, sulphur.

The properties examined in this work were: the solubility of chalcopyrite through a suite of acid flux compositions, the effect of temperature and time on the solubility, and the optimum conditions under which the copper could be extracted from the flux/ore solid. A sample of chalcopyrite from the Horne Mine, Quebec was obtained for the following tests.

Solubility of Chalcopyrite in Flux

Preliminary work on the uptake of chalcopyrite with the acid flux demonstrated that a flux containing potassium persulphate alone was not effective but that some quantity of chloride was required to solubilize the chalcopyrite. Results of the present work are shown in Table 2 and plotted in Figure 3. The maximum uptake of chalcopyrite was approximately 94 mg Cu in 3 grams of flux (Figure 3), and was determined for the flux composition containing 10% sodium chloride. That is, a 3.0% Cu (94 mg) metal uptake, equivalent to a 9.0% solubility of chalcopyrite in the flux, assuming the chalcopyrite sample was stoichiometrically $CuFeS_2$.

As this result was lower than had been anticipated, the aggressiveness of the flux towards pure copper metal was evaluated. The uptake of a flux containing 20% sodium chloride/80% potassium persulphate was found to be approximately 300 mg Cu metal per 3 gms of flux (10% by weight uptake of copper). It is apparent that the capacity of the flux for copper is much greater than was implied by the results found when fusing chalcopyrite. Some proportion of the aggressivenes of the flux was therefore being consumed in other reactions (e.g. evolution of sulphur gas). This assumption was verified by observing sulphur condensate on the walls of the reaction vessel when chalcopyrite was fused with the acid flux. The evolution of native sulphur could be regarded as an economic by-product; the quantity of the condensate in terms of its value was not pursued.

The Effect of Temperature and Time on Solubility

The Lindberg furnace with a chromel-alumel thermocouple setup (shown in Figure 1) was used for the following experiments. The furnace was preheated to a selected temperature. When the furnace stabilized the sample contained in the pyrex reaction vessel was lowered into the furnace and held at the selected temperature setting for a desired time. Each sample removed from the furnace was dissolved in 100 ml 2N HCl and subsequently centrifuged. The resulting

clear blue solutions were then analyzed with the Scintrex atomic absorption spectrophotometer, the AAZ-2. The results are given in Table 3 and are plotted in Figures 4 and 5.

As the time in the furnace at 639°C was increased, the quantity of copper solubilized did not vary significantly. However, as the temperature increased, the quantity of solubilized copper increased. The errors inherent in the experimental design (e.g. temperature fluctuations associated with the furnace setup) and the variation in ore composition may account for the small amount of scatter observed.

Optimum Leach Condition Experiment

In the present context, the optimum leach solution referred to that solution which best solubilized the cooled flux and allowed optimal separation of the desired metal component from other waste fractions. Eh-pH diagrams (Pourbaix, 1966) were consulted in order to predict the form of a given element in an aqueous solution. Application of the data contained in these diagrams is limited by the reactions which have been considered in establishing them; that is, in general, they are valid only in the absence of complexing agents.

Samples of 250 mg chalcopyrite in 3 grams of flux (10% sodium chloride/90% potassium persulphate) were fused and dissolved with 50 ml water, 0.1N H_2SO_4, 0.5N H_2SO_4 and 1.8N H_2SO_4. In each case, the cooled melt was easily dissolved, and resulted in a clear blue solution. The optimum leach solution following the fusions should likely be a very weak acid solution, in order that the hydrolysis pH of iron not be reached. The minimum quantity of acid solution required for complete solubilization was not considered.

ILMENITE

The problems faced in the processing of ilmenite today are the dwindling supplies of titanium dioxide (rutile reserves) for direct introduction into the chlorination process and the disposal of waste acid solutions from the sulphination process. Canadian ilmenite slag cannot, at present, be processed by chlorination due to the level of impurities (e.g. oxides of magnesium, calcium and iron). It would be beneficial, therefore, to either offer an alternative process to the present day sulphination process in the light of eliminating the enormous disposal problems associated therewith, or to offer an acceptable ilmenite concentrate which could be classified as "synthetic rutile" for the chlorination process.

The ilmenite/flux mixtures were characterized with respect to solubility of the mineral in the flux, time and temperature dependency of solubility and optimum leach conditions of the cooled solid. A sample of titania "slag #3" was obtained from QIT-Fer et Titane Inc., through Hatch Associates. In this set of experiments, the terms titania slag and ilmenite are used interchangeably.

Solubility of Ilmenite in the Flux Components

A range of flux compositions from 0% sodium chloride/100% potassium persulphate to 100% sodium chloride/0% potassium persulphate were studied. Three gram samples, fused with 500 mg of titania slag were dissolved in 2N HCl acid solution and analyzed for titanium uptake by light absorption colorimetry using chromotropic acid as the complex for titanium (Feigl 1972, pg 489). The results of the solubility determination are presented in Table 4 and plotted in Figure 6.

The flux containing only potassium persulphate was the most aggressive for the decomposition of the slag. The solubility of the titanium in 3 grams of persulphate was found to be approximately .262 gms (8.7% solubility).

The Effect of Temperature and Time on the Solubility

The same experimental setup used for chalcopyrite (Figure 1) was used for the titania slag. The sample size used in these experiments was 3 grams flux with 700 mg slag. Each sample removed from the furnace was dissolved in 100 ml 2N HCl and subsequently filtered. The resulting solutions were then analyzed by light absorption colorimetry.

The results are given in Table 5 and are plotted in Figures 7 and 8. The uptake of titanium did not increase or decrease with time or temperature. The decomposition action by the flux towards the titania slag appeared, therefore, to be most active during the initial gas evolution stage. It is also possible that the flux was exhibiting a solubility limit for titanium.

Optimum Leach Condition Experiment

As described previously, the Pourbaix diagrams were consulted as a guide in determining the most suitable leaching conditions for copper, titanium and niobium. The Pourbaix diagram for titanium shows that titanium is appreciably soluble in acid solution. Work was therefore initially conducted using a weak acid solution to represent a low cost solvent.

Samples of 250 mg titania slag in 3 grams of flux (100% potassium persulphate) were fused and dissolved in 50 ml 0.1N H_2SO_4, 0.5N H_2SO_4, 2N H_2SO_4, 3.6N H_2SO_4 and 3.6N H_2SO_4. A cloudy solution would result initially, which appeared to contain a hydrate presumed to be $TiSO_4.H_2O$. This hydrate was insoluble in water but soluble in weak acid. A weak acid solution (0.1N H_2SO_4) would appear to be adequate for dissolution of the flux/mineral solid. Future studies would be instrumental in indicating the quantity of acid required for complete solubilization on a pilot plant scale, as well as a method for precipitating the titanium from solution without coprecipitating the iron contained in solution.

PYROCHLORE

The decomposition of pyrochlore by digestion with hydrofluoric acid is a process which requires sophisticated equipment and precautions. The use of the acid flux was investigated as an economic and less hazardous alternative for the extraction of niobium. The solubility of pyrochlore in the flux, time-temperature solubility dependence and the optimum leach solutions were evaluated. A sample of ore concentrate was obtained from SOQUEM.

The pyrochlore concentrate was analyzed by x-ray fluorescence and the results are summarized in Table 8. The laboratory reports are given in Appendix IV. The major components of the ore were found to be: niobium, calcium, sodium, titanium and fluorine. The total of all components was, however, only 70-80%. The unidentified 20-30% could have been indicative of an additional mineral not accounted for in the analysis. By averaging the results of the two analyses of the raw ore, and assuming the 20-30% fraction not accounted for was not significant to the structural components, the chemical formula could be written as:

$$(Ca_{.47}\ Na_{.7})Nb_2O_6F_{0.8} \qquad FW = 330\ g/mole$$

Solubility of Pyrochlore in the Flux Compositions

Colorimetric techniques for the determination of niobium in aqueous solutions were not successful due to iron and calcium interferences. A sieving technique was therefore employed to separate the niobium oxide from unreacted pyrochlore. The pyrochlore used in these experiments was a -100, +200 mesh fraction. Any -270 mesh material after fluxing and solubilization was then believed to represent the chemical precipitate, Nb_2O_5.

Two gram samples of pyrochlore were fused in a suite of flux compositions and subsequently dissolved in deionized water yielding a solution containing unattacked pyrochlore and a fine white precipitate. This solution was screened through the 270 mesh. The +270 mesh material was assumed to be "unattacked pyrochlore", while the -270 mesh fraction was classified as the chemical precipitate containing niobium oxide, partially attacked pyrochlore and possibly calcium sulphate. Weighed samples of the -270 mesh were also digested in 2N HCl acid for 2-3 hours in order to perfect the crystal structure of the precipitated oxide, and to further separate any soluble impurities (e.g. calcium sulphate, iron). The data are given in Table 6 and are plotted in Figure 9.

The results indicated an increase in aggressiveness of the flux towards pyrochlore, as the sodium chloride content was decreased. In particular, the flux composition containing 10% sodium chloride/90% potassium persulphate appeared to attack the pyrochlore to the greatest extent. The reason for this may have been that a small amount of chloride totally evolved as oxychloride or chloride gas enhancing the aggressiveness of the flux. Higher levels of sodium chloride may have introduced an additional chloride component in the melt which reduced the oxidation potential of the flux.

The -270 mesh weights did not show a systematic variation with flux composition. However, after digesting the samples in hydrochloric acid, the weights of the insoluble material did show a trend matching the weights of the pyrochlore taken up by the flux (Figure 10). The reason for this trend will be discussed in the next section.

Test for Calcium Sulphate in Precipitate

The soluble fraction of the precipitate was determined to be calcium sulphate. The colorimetric determination of calcium from leach solutions prepared from pyrochlore/flux fusions was conducted by a titrative technique. A test kit was obtained entitled "Hardness Titration EDTA Method" from Quatic Chemicals Limited (Guelph, Ontario). The test was carried out on a series of pyrochlore/flux leach solutions (e.g. flux compositions ranging from 0% sodium chloride/100% potassium persulphate to 80% sodium chloride/20% potassium persulphate).

The uptake of calcium remained approximately constant (0.27 gms $CaCO_3$/100 ml/ 800 mg pyrochlore fused) which tended to indicate that the solubility limit of calcium sulphate in the leach solution was reached and the excess precipitated with the niobium oxide (also indicated by the digestion test results shown in Table 6).

Time-Temperature Solubility Experiments for Pyrochlore

The experimental setup was identical to that used for the chalcopyrite and ilmenite as shown in Figure 1.

A range of pyrochlore/flux samples was fused for varying times at some given temperature and varying temperatures for a constant time. Each sample was then dissolved in water and screened through the 230 mesh. Both fractions, +230 mesh and -230 mesh, were collected and weighed. The precipitate (-230 mesh) was subsequently digested in 2N HCl and reweighed. The data from both experiments are given in Table 7 and are plotted on Figures 11 to 14.

As both time and temperature in the furnace were increased, the quantities of pyrochlore attacked and fines precipitated showed some scatter but remained relatively constant. Under the present experimental conditions, therefore, the time and temperature in the furnace were not interpreted to be contributing factors to the variable solubility of the pyrochlore/flux mixture.

Visually, however, the +230 mesh fraction appeared bleached for the higher temperatures and longer furnace times. After digesting this "unattacked pyrochlore" material, an average loss in weight of 15% was experienced. The bleaching effect may have been due to the presence of calcium sulphate "clumps" or another fusion product resulting in an apparently higher fraction of coarser material not passing the 230 mesh.

To determine whether this material was residual unattacked pyrochlore, three samples were sent to the Royal Ontario Museum for x-ray diffraction analysis. The report is attached as Appendix II. The unidentified white constituent was

amorphous and was believed to be a reaction product of the fusion process. The scatter in the time-temperature solubility data may therefore have been a result of the entrapment of some of the chemical precipitate during the screening process. The solubility of the pyrochlore concentrate in the flux may therefore have been greater than was determined.

Optimum Leach Methods for the Solubilization of Flux/Pyrochlore Solid

As discussed previously, optimum leach solution referred to that solution which best solubilized the cooled flux and allowed optimal separation of the desired metal component from other waste fractions.

The dissolution of niobium metal is difficult. It is not attacked by common acids such as HCl, H_2SO_4 and HNO_3. It can be attacked by concentrated HF acid. Solubilization of the niobium-bearing melt with water will precipitate niobium oxide. In order to prevent the hydrolysis of other metal ions (e.g. iron, manganese, calcium, etc.) the leaching solution should also contain some quantity of acid.

a) Precipitation of Niobium Oxide by Leaching with Water

Niobium oxide precipitate was prepared fusing samples of flux (10% NaCl/ 90% $K_2S_2O_8$) with pyrochlore and dissolving the cooled melt in water and screening to separate the fine white precipitate from the "unattacked pyrochlore". The precipitate was subsequently digested in 2N HCl. One sample of the digested precipitate was ignited. Several samples of the precipitated niobium oxide were analyzed by x-ray diffraction and x-ray fluorescence in order to determine the degree of purity.

The x-ray diffraction analysis was conducted at the Mineral Sciences Laboratory of Energy, Mines and Resources, Canada. A copy of this report is enclosed as Appendix III. Hand mixed niobium oxide/pyrochlore samples were analyzed for comparison. Also included in this report are electron micrographs of polished sections prepared from the leach residue. The x-ray diffraction analysis indicated the presence of pyrochlore grains and an amorphous phase, believed to be another form of niobium oxide. The photomicrographs showed that the composition of the leach residue was not homogeneous consisting of niobium, potassium and sulphur (in the form of a compound) with minor to trace amounts of of titanium and chlorine. Calcium, iron, aluminum and silicon occurred in random and trace amounts. It was apparent therefore that together with the precipitated niobium, small amounts of unattacked pyrochlore as well as some undissolved fusion solid were present.

The x-ray fluorescence results of the niobium oxide precipitate are presented in Table 8. Also included in this table are two analyses of the pyrochlore concentrate for comparison (a copy of the laboratory report of these results is enclosed in Appendix IV). The analyses of the precipitated niobium samples were comparative, except for the quantity of niobium oxide reported. The difference in percentage was reflected in the loss on ignition (18.5%) determined for the sample which was not ignited. The titanium oxide from the raw ore appeared to

be precipitating with the niobium in this method of extraction. Small amounts of the other oxides found in the precipitate, e.g. sodium, potassium, calcium, iron, may have been due to the presence of residual pyrochlore which was contaminating the precipitate and which could not be discriminated by x-ray fluorescence.

In conclusion, the precipitated niobium material from a sample of pyrochlore concentrate contained residual, unattacked pyrochlore grains and some quantity of coprecipitating metal oxide impurities. Crushing of the cooled melt to ensure greater surface area contact of flux components with aqueous leach solution, and a greater separation between the original mesh size of the pyrochlore and the mesh size used to separate the final product would likely upgrade the precipitated product.

b) Solubilization of Pyrochlore/Flux Fusion Product with Oxalic Acid

A second method of solubilizing pyrochlore/flux fusion products was evaluated. Oxalic acid and ammonium oxalate have been used by other workers to keep niobium and tantalum in solution (Busev, 1970). A series of niobium-bearing solutions were made by fusing both pyrochlore and pure niobium oxide, followed by dissolution of the cooled solids with a 2% oxalic acid solution. The niobium was solubilized rather than precipitated. Specifically, four solutions were prepared by fusing 1.5 grams flux (10% sodium chloride/90% potassium persulphate) in test tubes containing 250 mg pyrochlore, 150 mg pyrochlore, 200 mg niobium oxide and 100 mg niobium oxide, respectively. The cooled solids were then dissolved in 150 ml 2% oxalic acid solution and diluted to 200 ml with deionized water. These solutions were sent to X-Ray Assay Laboratories for analysis by emission spectroscopy (Direct Current Plasma). A copy of the test results are given in Appendix IV and summarized in Table 9. The pyrochlore solutions were analyzed for iron, niobium, tantalum, titanium and calcium and the standard solutions for niobium. The results of the analysis of the standard solutions (pure Nb_2O_5) showed a 100% uptake of niobium by the oxalic acid. Similarly, the analysis of the pyrochlore solutions appeared to demonstrate a 100% solubility of niobium in the oxalic acid (assuming the ore concentrate contained 58% Nb_2O_5). Calculations are given in Appendix V.

Aqueous Leaching of Pyrochlore/Flux Solids:

The aqueous solubility of potassium persulphate increases with temperature (CRC Handbook, 1973). Therefore, the effect of temperature on a persulphate-bearing flux with and without pyrochlore was evaluated.

Two samples were prepared by fusing 0.2 grams of pyrochlore with 1.2 grams flux (10% NaCl/90% $K_2S_2O_8$) in a crucible. As a control, 1.2 grams of flux (10% NaCl/ 90% $K_2S_2O_8$) was also fused. Each sample was subsequently placed in 200 ml deionized water and mechanically stirred. One sample of flux/pyrochlore was heated to approximately 70°C while stirring and the other was stirred at room temperature.

At room temperature the sample containing the flux components only dissolved within approximately 10 minutes, whereas the samples containing pyrochlore/flux fusion products did not completely dissolve after an 8 hour period. No notable

gain in solubility could be observed in the sample which was heated. The ability of the fusion product to dissolve in the aqueous leaching step, therefore, was not simply a function of the solubility of the individual components. On an industrial scale it may be worthwhile to blow gas through the cooling melt in order to increase surface area contact of the fusion products.

Decanting Experiment

When fusing pure niobium oxide with certain flux compositions, the reaction appeared to be complete when a clear gold coloured melt was obtained. However, following this stage, the niobium reprecipitated in the melt. The purpose of this experiment, therefore, was to investigate the possibility of allowing the niobium to precipitate in order that the molten flux (containing all contaminating components from the original ore) be decanted from the precipitated niobium oxide.

Precipitation of niobium in the melt occurred for fluxes containing greater than 30% by weight sodium chloride, whereas the greatest solubilization of the niobium in the melt occurred with fluxes containing very little or no sodium chloride. Possibly, the presence of the sodium chloride caused the formation of niobium oxychloride, which then decomposed to the more stable niobium oxide compound.

The optimum flux composition for the occurrence of reprecipitation in the melt was found to be 40% sodium chloride/60% potassium persulphate. A pyrex crucible containing 1.0 gram niobium oxide in 9 grams flux was fused to a clear melt. Precipitation of the niobium in the melt yielded a homogeneous flux/precipitate mixture. The fact that the niobium remained suspended in the melt left the possibility that the flux could be decanted away from the insoluble gangue minerals. However, upon prolonged heating the mixture solidified preventing separation. The decanting process did not, therefore, appear to be feasible, at least with the present experimental design.

Use of Sodium Persulphate in Substitution for Potassium Persulphate

The substitution of sodium persulphate for potassium persulphate as a flux component was suggested for two reasons: a) the waste products generated by a sodium salt may be less hazardous and thus more readily disposed, and b) sodium persulphate purchased in bulk quantities may be less expensive than potassium persulphate. A series of fusions were therefore conducted examining how the use of sodium persulphate would differ from potassium persulphate.

Sodium persulphate reacted in a very similar manner to potassium persulphate. For example, compositions containing higher levels of sodium chloride also precipitated niobium in the melt. Secondly, when fusing pyrochlore, a small amount of sodium chloride was required in the flux in order to obtain a molten sample upon heating. However, a slightly higher quantity of sodium chloride was required in the case of the sodium persulphate flux.

The use of sodium persulphate and its effect on the solubility of the pyrochlore or niobium oxide in the melt was not determined analytically. However, upon visual observation, the solubility of niobium oxide or pyrochlore in the sodium persulphate flux was somewhat lower than in the potassium persulphate flux. Since it was expected that there would be very little difference between the sodium and potassium fluxes, it is possible that the sodium persulphate, which is not a commonly used laboratory reagent, may have been old stock and may have degraded during storage.

The solubility of the cooled sodium persulphate melts was noticeably greater than the equivalent potassium persulphate fusions.

COST EVALUATION

1.0 THE EVALUATION IN BRIEF

The Scintrex fluxing process has been the subject of a testing program in the Scintrex laboratories, over the past several months. The result of the various test studies have been reported month by month in progress reports, which we have followed and on which we have commented from time to time.

In February, we studied the reclamation of potassium from waste solutions and its reconversion to potassium persulphate; from that study, two major facts emerged:

1. Potassium recycle would probably be highly beneficial to costs.

2. The cost of potassium persulphate, even home-made, is overwhelmingly the most significant part of the total costs.

Comparison of the cost of the required potassium persulphate with present commercial total costs of processing ilmenite, chalcopyrite, or pyrochlore show that the fluxing route would be much more costly, and therefore is unlikely to be of commercial interest.

2.0 THE AMOUNT AND COST OF KPS NEEDED

The test studies have (properly) used various ratios of flux to mineral, and various flux compositions. The desireable compostion appears to be 10% NaCl, 90% KPS. Assuming that ratio, the KPS to mineral ratios reported have been:

	July	Nov	Dec	Jan	Feb	X
Pyrochlore		3.2	2.7	5.4	5.4	2.7
Chalcopyrite	6.7		10.8	6.7		6.7
Ilmenite		3.8	12.0			3.8

For cost evaluation, consider the ratios under X above.

The price of KPS, as purchased, was quoted in January at Can. $1.85/kg. The cost of KPS produced on site by internal recycle of potassium was projected at $1.00/kg (plus the cost of makeup chemicals). Taking $1.00/kg, the cost of KPS for the fluxing process would be:

Pyrochlore (60% Nb_2O_5)	Over $4.00/kg Nb_2O_5
Chalcopyrite (35% Cu)	Almost $20.00/kg Cu
Ilmenite (55% TiO_2)	Almost $7.00/kg TiO_2

3.0 MODERN PROCESSING OF NIOBIUM MINERALS

The coming of solvent extraction (SX), as a metallurgical process has led to a great change in the processing of niobium and tantalum minerals. With the elements in a proper solution, the elimination of impurities and the separation of the two elements becomes very "simple" in the SX circuits. Both elements can be produced to high purity by simple and inexpensive SX scrubbing routines.

The solution required in the SX process is high in fluoride, and is produced by leaching (dissolving) the niobium mineral in a mix of hydrofluoric and sulphuric acids. The costs associated with the process can be less than \$1/kg Nb_2O_5 for chemicals and energy - or less than a quarter of those for the fluxing route.

4.0 PRESENT ILMENITE PROCESSING

In the common industrial process for processing ilmenite into pigment, the mineral is first mixed batchwise in large tanks with sulphuric acid of around 90% strength. In due course the contents of the tank undergo a violent reaction, with rise in temperature, vapour emission, and a "setting up" into a porous solid mass. The solid mass is then dissolved out with water. The acid used cannot be economically reclaimed from the final waste solutions, in which its strength is down to about 20%. Dealing with the waste acid is not yet universally required (dumping at sea is still practiced) but soon will be. When it is necessary, the common method is neutralization with lime - all of which adds at most about \$0.20/kg TiO_2 to processing costs. Total costs of processing ilmenite to finished pigment are considerably less than the costs of KPS alone cited earlier here.

5.0 PROCESSING CHALCOPYRITE

Total smelter costs in processing copper today do not exceed \$0.50/kg copper.

6.0 ALTERNATE FLUX COMPOSITIONS

A number of the salient facts about the chemistry and economics of the Scintrex fusion process lead us to wonder about alternate flux compositions:

1. The oxygen generated in fusing the persulphate is largely lost from the melt and plays no stoichiometric role in the reactions.

6.0 ALTERNATE FLUX COMPOSITIONS (cont'd)

2. The melt, after escape of the oxygen becomes a pyrosulphate melt.

3. Pyrosulphate is made commercially by fusion of bisulphate.

4. The chemical cost of persulphate fusion is higher than can be borne on the minerals evaluated so far.

A large part of the cost of persulphate arises from the electrolysis step in manufacture.

These facts suggest the possibility that fluxes with some proportions of persulphate, pyrosulphate, and bisulphate might be interesting technically and economically.

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AGWL/cdb

Comments on Economic Considerations

The major conclusion was that the fluxing route as described would not be of commercial interest for any of the three ores. The values used in this evaluation were based on the quantity of flux/mineral used in a particular experiment rather than actual solubility data.

Using experimental solubility data, the KPS/mineral ratios were: chalcopyrite, 10.0 (approx.); ilmenite, 7.5 (approx.) and pyrochlore, 3.4. The ratios used by Hatch were 6.7, 3.8 and 2.7 respectively. In all cases the ore values used by Hatch were greater than indicated by solubility data. The cost estimates are therefore lower than if the solubilities were used.

In considering the suggestion for alternate flux compositions (e.g. pyro-sulphate, bisulphate), we should note previous work conducted in this laboratory has shown that the oxygen generated from persulphate plays a significant role in the effectiveness of the solubilization of some of the metals (e.g. gold). However, this may not be true in all cases. Consideration of alternate flux compositions may therefore warrant further study.

SUMMARY AND CONCLUSIONS

The present research program has been concerned with the application of an oxidizing flux for the decomposition of chalcopyrite, ilmenite and pyrochlore.

Initially the pure flux components were characterized. A binary phase diagram was generated for the two component flux showing a peritectic at 45% NaCl/55% $K_2S_2O_8$ and a eutectic at 25% NaCl/75% $K_2S_2O_8$. In the region of 0 to 18% NaCl a finer structure was detected but was not clearly understood in these experiments. The fluxes with the lowest melting points contained less than 25% NaCl. The gases evolved from a 50/50 mixture of the NaCl and $K_2S_2O_8$ were found to be oxychloride or chloride with a trace of SO_2. The solid after fusion was determined to be a chloride-sulphate mass.

All three ores were best solubilized with flux compositions containing less than 10% sodium chloride. This coincides with some of the lowest melting flux compositions on the phase diagram.

The solubility of copper from chalcopyrite in the flux was found to be approximately 3% (for higher fusion temperatures, this value was increased by approximately 1-2%). This is equivalent to a 9% uptake of chalcopyrite, assuming the chalcopyrite to be stoichiometric. The fusion products were easily solubilized in a weak sulphuric acid solution. The use of a potassium persulphate flux, in the quantity required for the decomposition of chalcopyrite, does not seem economically feasible for the current North American market.

The solubility of titanium from ilmenite concentrate in the persulphate flux was determined to be 8.7%. The cooled fusion products were also easily dissolved in weak acid solutions. Although the solubility of the ilmenite in the persulphate was somewhat higher than in the case of the chalcopyrite, the present cost of potassium persulphate, and the present objectionable disposal problems of acid leach solutions, would also render this route of ilmenite decomposition uneconomic.

The solubility of pyrochlore in the flux was much higher (27% by weight) than chalcopyrite or ilmenite. This solubility may further increase for longer fusion times and elevated fusion temperatures. The fusion product could either be solubilized with water to produce a niobium oxide precipitate, or with oxalic acid to produce a niobium complex in solution. From the present experimental work, the preferred leach was oxalic acid. By solubilizing the niobium it could be separated from any residual gangue minerals. Although at present the cost of potassium persulphate is too great for this process to be implemented on an industrial scale in Canada, future raw material limitations (e.g. supply and cost of hydrofluoric acid) and/or remote deposit localities may permit a reconsideration of the economics of this process.

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FIGURES AND TABLES

APARATUS USED FOR EXPERIMENTS REQUIRING CONTROLLED HEATING AND/OR COOLING

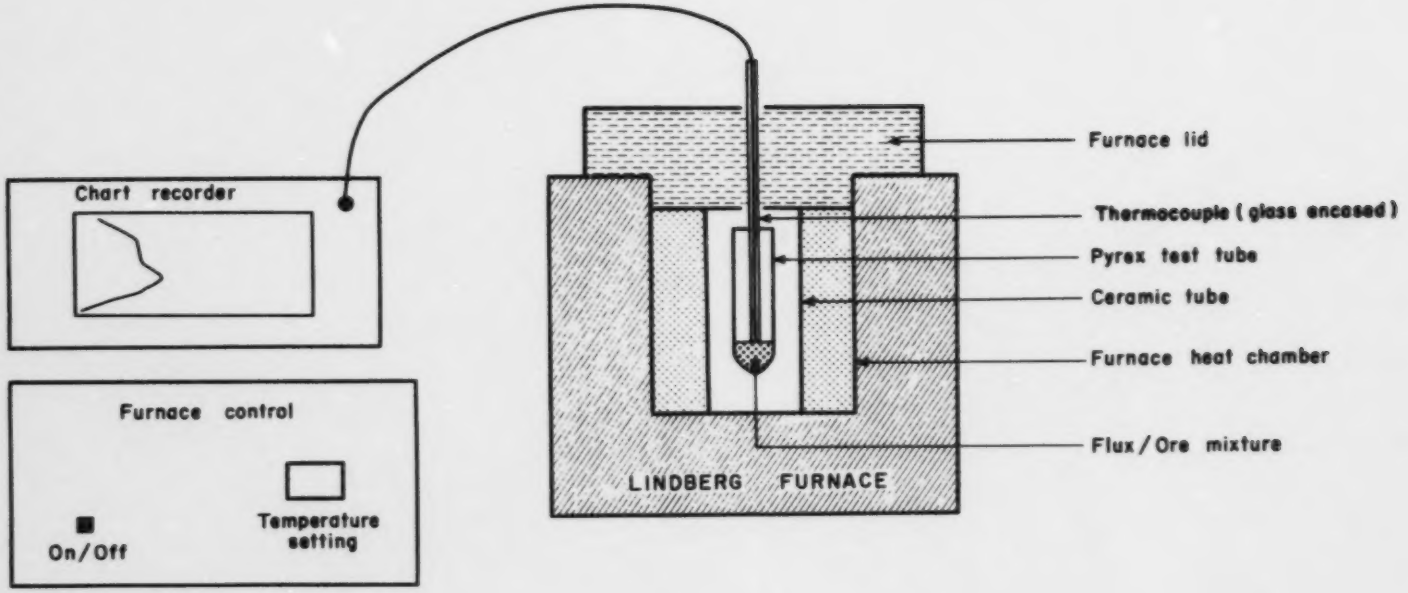


Figure 1

Table 1: **COOLING CURVE "BREAK" POINTS**

% NaCl	Temperature (°C)	Temperature Corrected for Eutectic at 424.2°C (°C)
0	262.5, 404	
3	237.4, 360.6	
4	352.5	
5	351.5	
8	327.4, 413.1	
10	332.5, 418	
15	313.5, 440.8	
18	292.9, 424.2, 443.4	292.9, 424.2, 443.4
20	424.2, 434	424.2, 434
22	424.2, 434.3	424.2, 434.3
23	424.2, 425.2	424.2, 425.2
24	424.2	424.2
25	424.2	424.2
28	424.2, 459.6	424.2, 459.6
30	426.4, 473.9	424.2, 474.7
35	414.2, 485.5	424.2, 497.2
40	418.0, 512.1	424.2, 519.6
42	416.1, 497.9, 514.1	424.2, 507.6, 524.1
44	416.1, 492.9, 545.4	424.2, 502.5, 556.0
45	420.2, 486.8, 566.6	424.2, 491.4, 572.0
48	419.2, 503.0, 572.7	424.2, 509.0, 579.5
50	417.0, 519.2, 580.5	424.2, 528.2, 590.5
55	419.0, 522.0 623.0	424.2, 528.5, 630.7
58	525.2, 641.4	
60	529.0, 649.0	
65	531.0, 685.0	

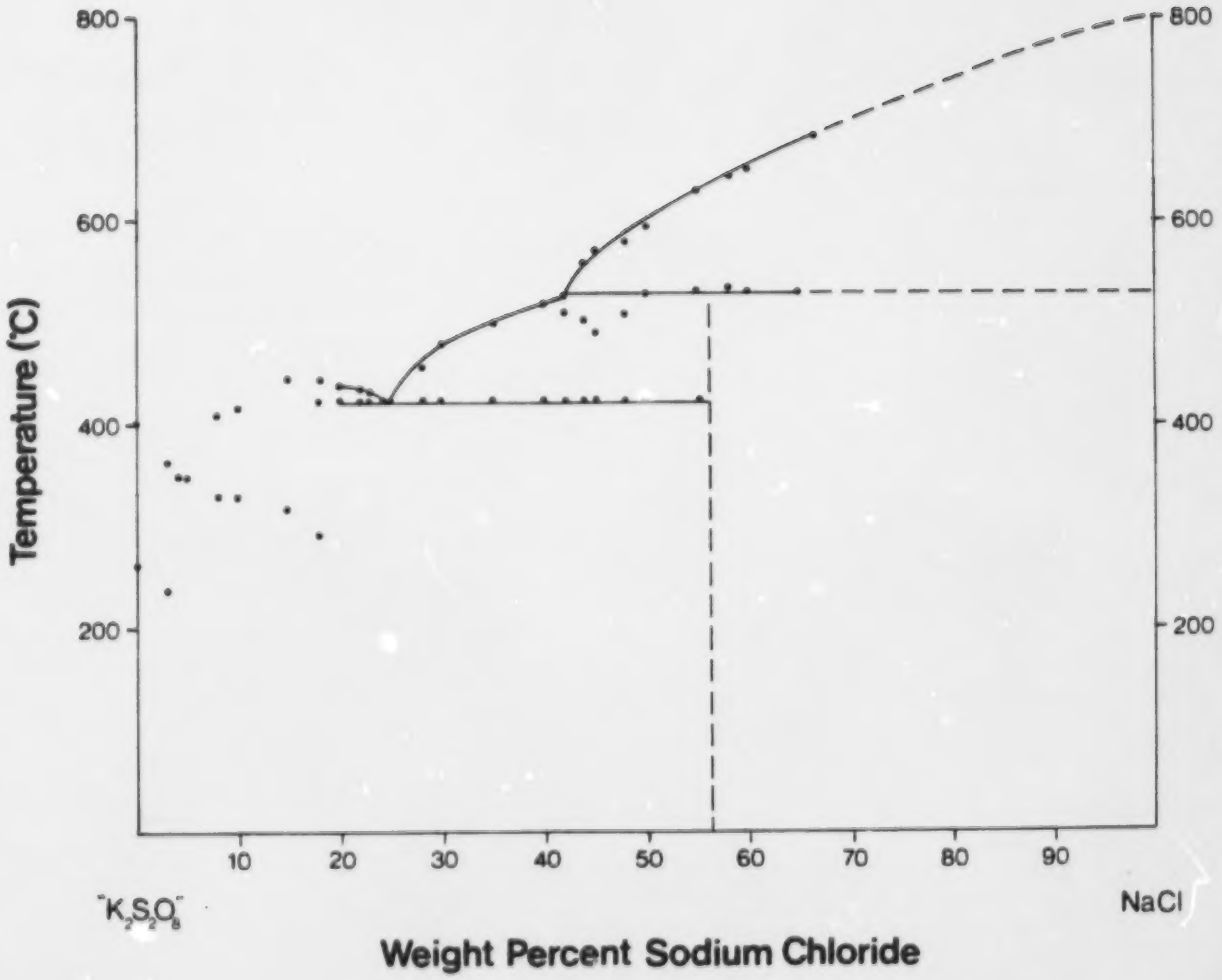

800
600
400
200
Temperature (°C)
10
20
30
40
50
60
70
80
90
"K2S2O8"
NaCl
Weight Percent Sodium Chloride

Figure 2

Table 2: **QUANTITY OF COPPER SOLUBLIZED BY FLUX FROM CHALCOPYRITE ORE**

	0%N 100%K	10%N 90%K	20%N 80%K	30%N 70%K	40%N 60%K	50%N 50%K	60%N 40%K	70%N 30%K	80%N 20%K	90%N 10%K	100%N 0%K
mg Cu	72.3	105.5	85.1	81.6	89.3	51.7	32.5	16.3	10.3	8.0	5.1

NaCl = N
$K_2S_2O_8$ = K
% by weight

Sample: 400 mg chalcopyrite/3 grams flux fused and dissolved in (0.1N) nitric acid

Analysis: Atomic Absorption (Scintrex AAZ-2 unit)

Data are plotted in Figure 3.

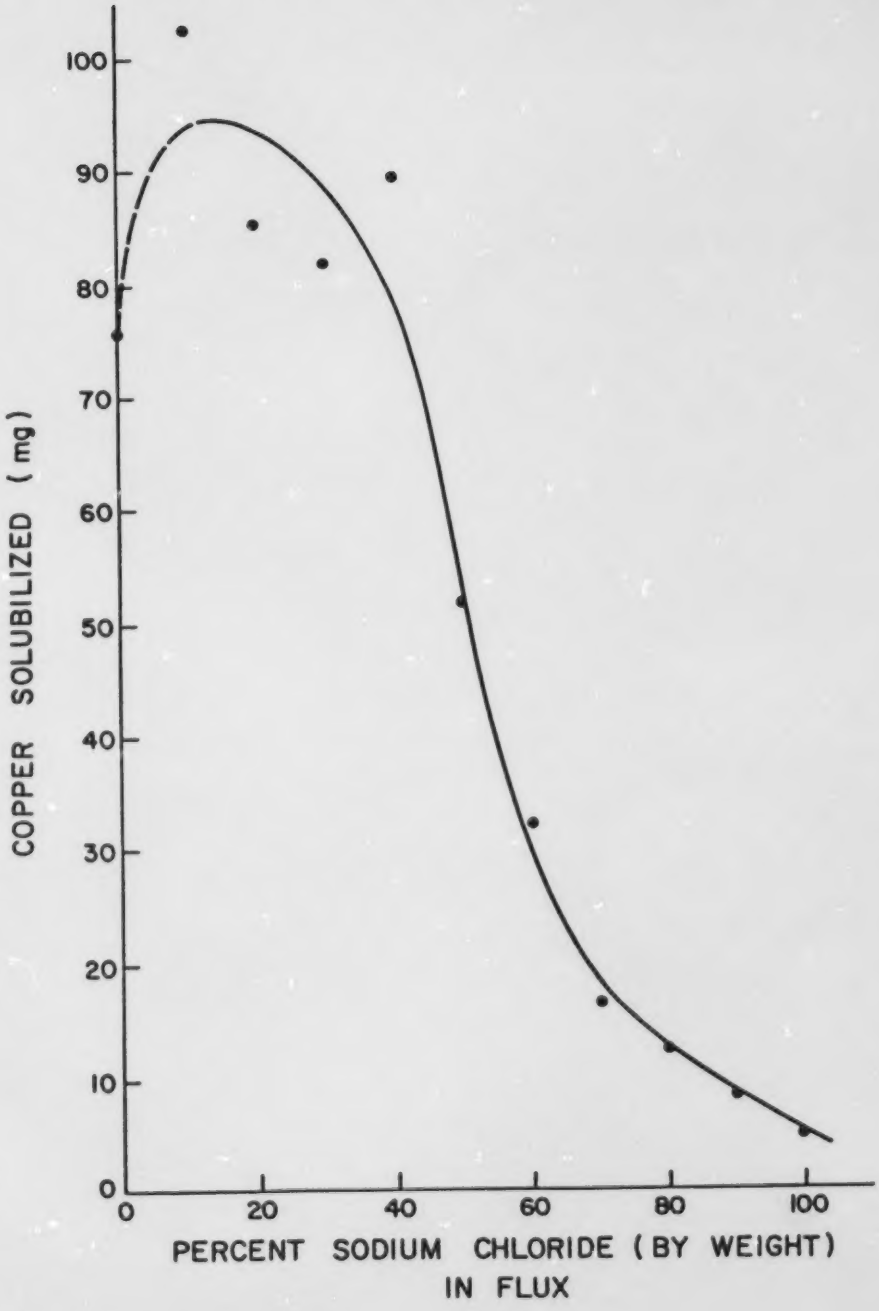


Figure 3
Copper Solubilized From Chalcopyrite as a Function of Flux Composition

Table 3: **TIME-TEMPERATURE SOLUBILITY EXPERIMENTS FOR CHALCOPYRITE**

Temperature Varying Experiment

Temperature (°C)	418	588	639	693	752	807
Time (min)	30	30	30	30	30	30
mg Cu	88.3	126.5	110.6	120.2	124.2	159.0

Time Varying Experiment

Temperature (°C)	639	639	639	639	639	639	639
Time (min)	7	15	30	45	60	120	180
mg Cu	116.9	120.0	110.6	113.9	116.1	105.8	133.2

Sample: 400 mg chalcopyrite/3 grams flux (20% NaCl/80% $K_2S_2O_8$) dissolved in 2N HCl

Analysis: Atomic Absorption (Scintrex AAZ-2)

Data are plotted in Figure 4 and 5.

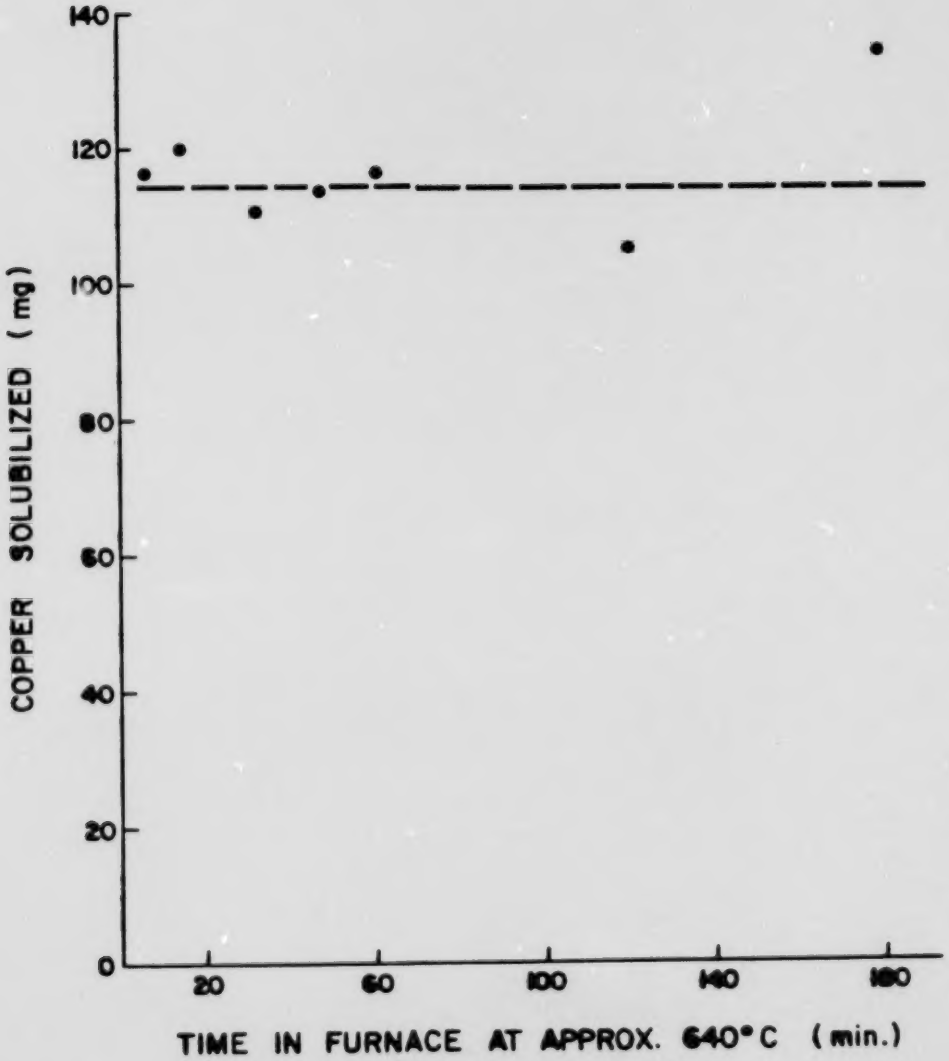


Figure 4
Copper Solubilized From Chalcopyrite as a Function of Fusion Time

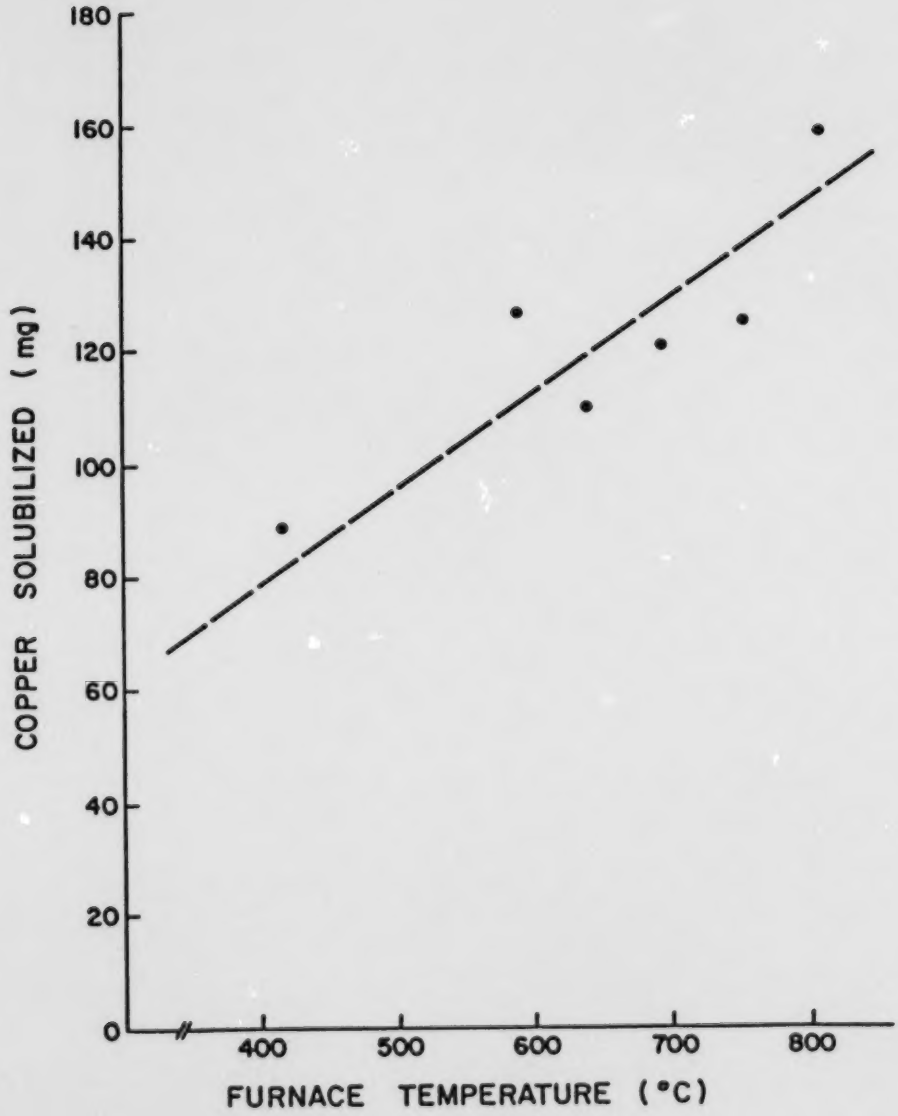


Figure 5
Copper Solubilized From Chalcopyrite as a Function of Fusion Temperature

Table 4: **QUANTITY OF TITANIUM SOLUBILIZED BY FLUX FROM ILMENITE SLAG**

	0%N 100%K	10%N 90%K	20%N 80%K	30%N 70%K	40%N 60%K	50%N 50%K	60%N 40%K	70%N 30%K	80%N 20%K	90%N 10%K	100%N 0%K
mg Ti	262	233	150	98.4	103.4	25.3	24.2	7.7	2.6	1.0	0.5

NaCl = N
$K_2S_2O_8$ = K
% by weight

Sample: 500 mg titania slag/3 grams flux and dissolved in HCl acid solution (2N)

Analysis: Light absorption colorimetry

Data are plotted in Figure 6.

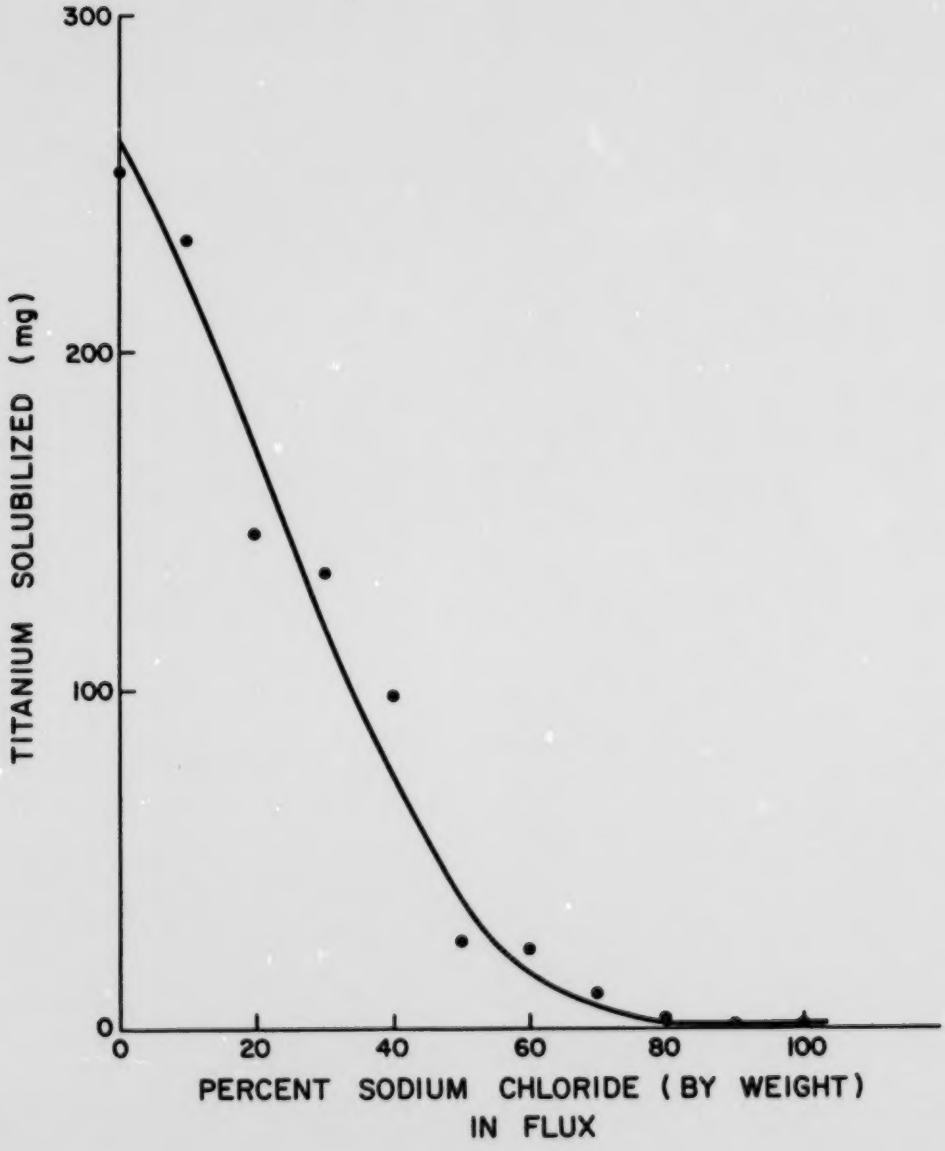


Figure 6
Titanium Solubilized From Ilmenite as a Function of Flux Composition

Table 5: **TIME-TEMPERATURE SOLUBILITY EXPERIMENTS FOR ILMENITE SLAG**

Temperature Varying Experiment

Temperature (°C)	575	634	688	698	747
Time (hr)	½	½	½	½	½
mg Ti	218	233	226	216	229

Time Varying Experiment

Temperature (°C)	634	634	634	634	634	634	634
Time (min)	6	15	27	45	60	120	180
mg Ti	279	274	275	258	275	275	243

Sample: 700 mg titania slag/3 grams flux (10% NaCl/90% $K_2S_2O_8$) and dissolved in 2N HCl

Analysis: Light absorption colorimetry

Data are plotted in Figures 7 and 8.

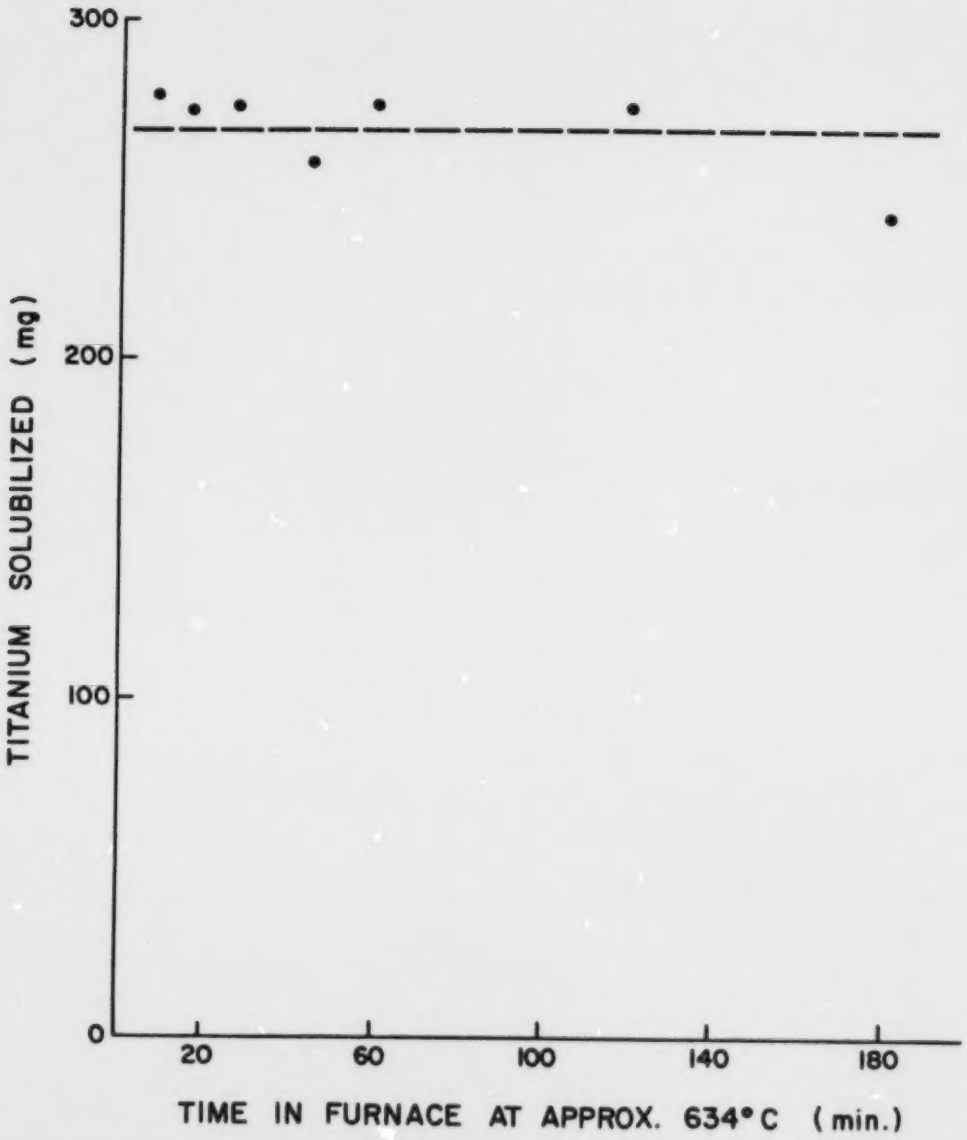


Figure 7
Titanium Solubilized From Ilmenite as a Function of Time at Fusion Temperature

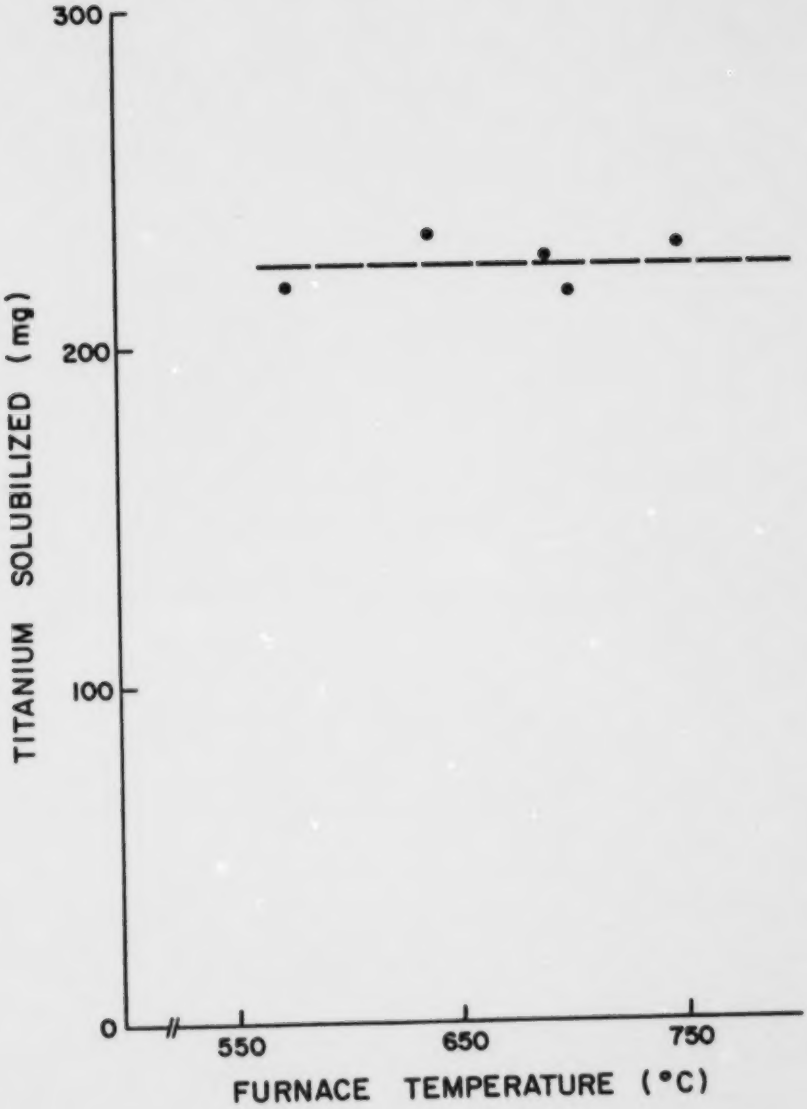


Figure 8
Titanium Solubilized From Ilmenite as a Function of Fusion Temperature

Table 6: **SOLUBILITY OF PYROCHLORE IN FLUX**

Starting Material: +270 mesh
Sample Size: 2.0 grams
Flux Sample Size: 6.0 grams (10% NaCl/90% $K_2S_2O_8$)

Flux Composition	* 0% N / 100% K	10% K / 90% N	20% N / 80% K	30% N / 70% K	40% N / 60% K	50% N / 50% K	60% N / 40% K	70% N / 30% K
Unattacked Pyrochlore (gms)	.57	.39	.49	.62	.94	1.38	1.37	1.5
Pyrochlore attacked by flux (gms)	1.43	1.61	1.51	1.38	1.06	0.62	0.63	0.50
Solids (gms) -270 mesh	1.50	1.60	1.24	1.26	2.08	0.70	0.62	2.23
Sample of -270 mesh Solids (gms) before digestion	2.857	2.937	1.240	1.260	2.010	0.682	0.618	0.856
Weight of Solids (gms) after digestion	2.022	2.63	1.03	0.938	0.688	0.355	0.271	0.071
% Solids After Dig. Before Digestion	70.8	89.5	83.1	74.4	34.2	52.1	43.9	8.3

In this table N represents NaCl
and K represents $K_2S_2O_8$

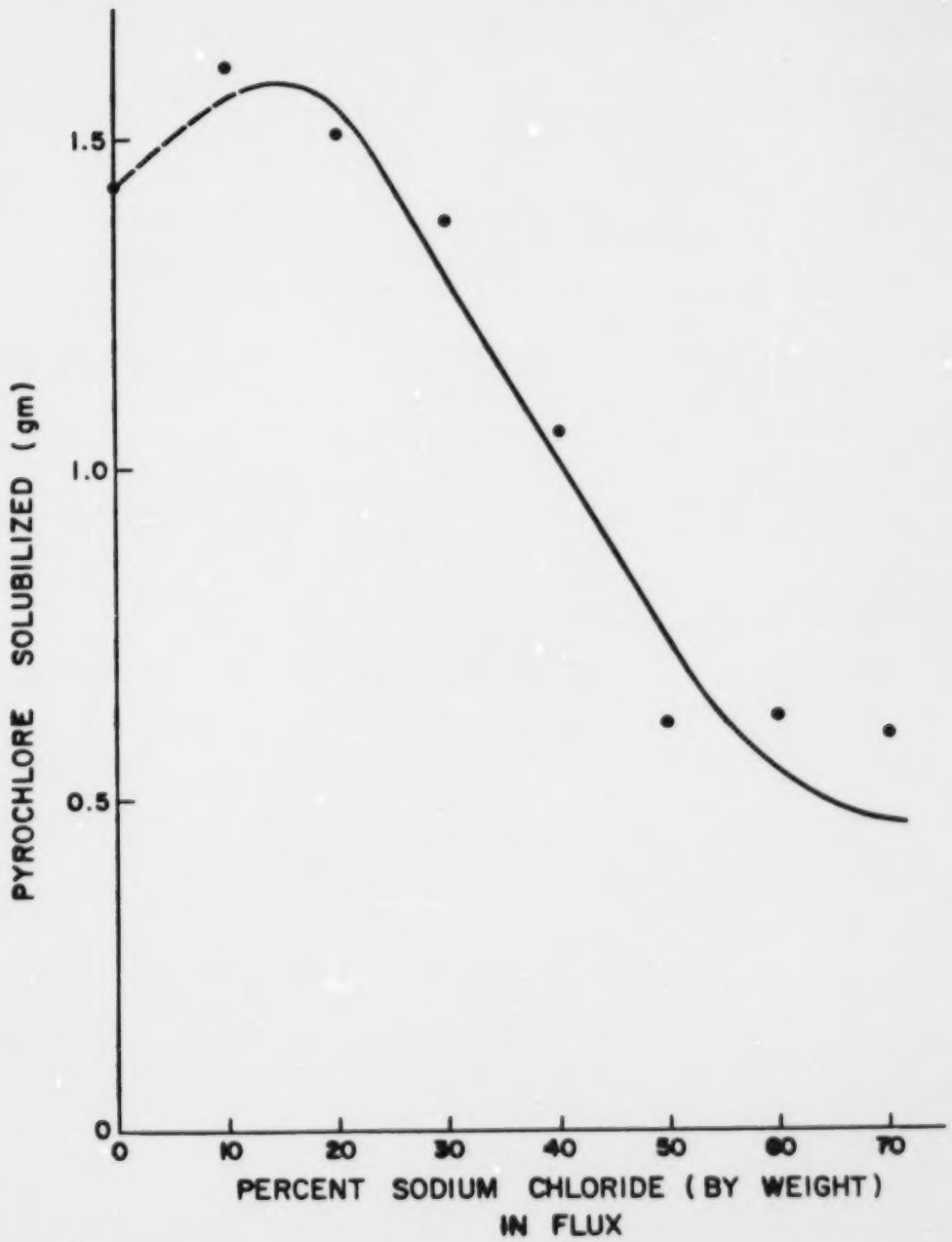


Figure 9
Pyrochlore Solubilized as a Function of Flux Composition

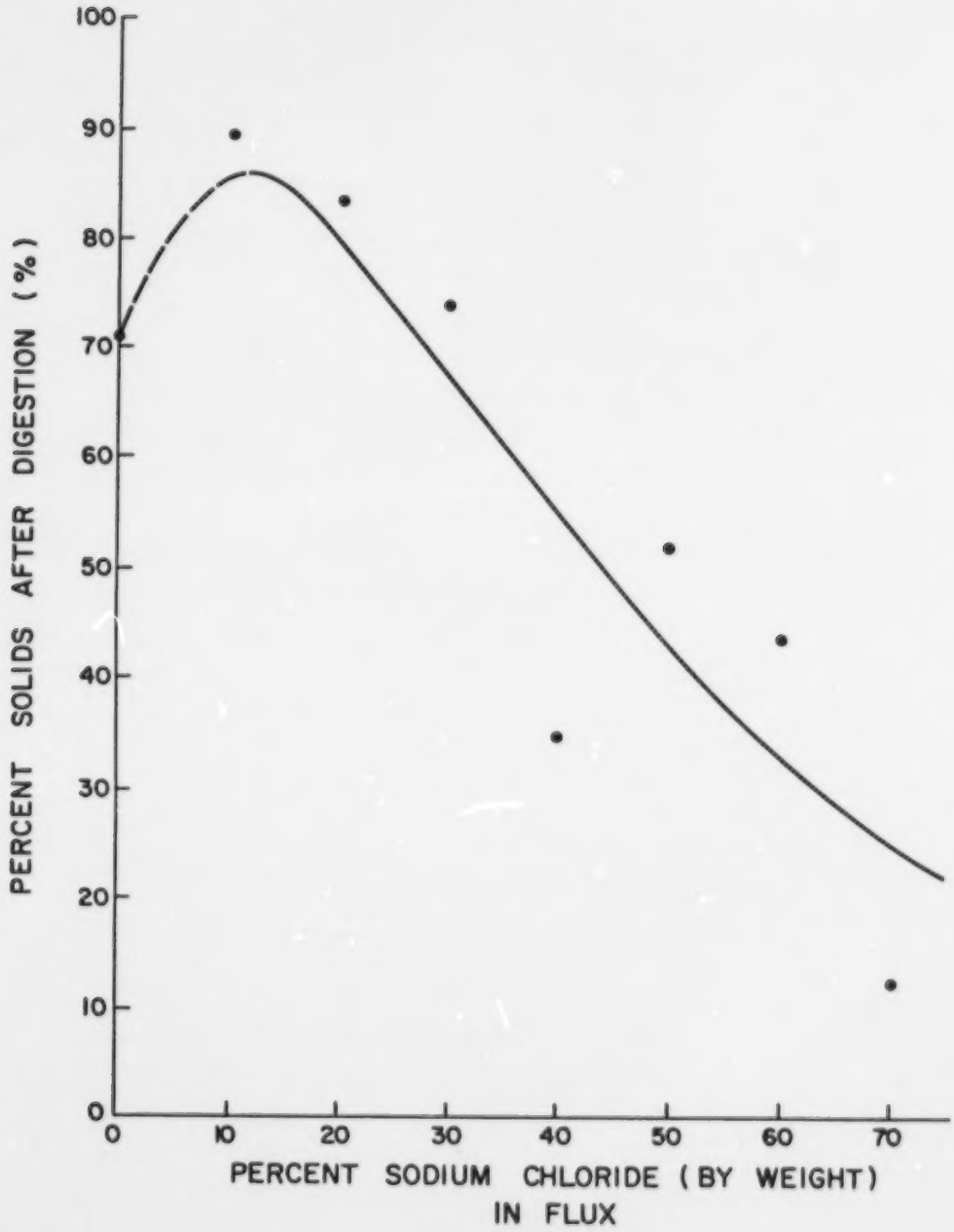


Figure 10
Niobium Precipitate Obtained as a Function of Flux Composition

Table 7: **TIME-TEMPERATURE SOLUBILITY OF PYROCHLORE**

Starting Material: +200 mesh
Sample Size: 2.0 grams pyrochlore
Flux Sample Size: 6.0 grams (10% NaCl/90% $K_2S_8O_8$)

	TEMPERATURE VARYING EXPERIMENT					TIME VARYING EXPERIMENT							
Temperature (°C)	532	605	612	666	727	600	600	600	600	600	600	600	600
Time (min.)	30	30	30	30	30	5	18	30	45	60	90	120	180
Unattacked pyrochlore (gms)	.664	.506	.668	.536	.510	.589	.498	.506	.527	.605	.641	.644	.538
Pyrochlore attacked by flux (gms)	1.336	1.494	1.332	1.464	1.49	1.411	1.502	1.494	1.473	1.395	1.359	1.356	1.462
Precipitate (-230 mesh)(gms)	1.067	1.270	1.224	1.131	0.99	1.179	1.208	1.270	1.18	1.346	1.111	1.493	1.162
Sample of -230 mesh fraction before digestion (gms)	0.877	1.225	1.208	1.066	0.886	1.07	1.164	1.225	1.18	1.189	0.968	1.493	1.162
Solids after digestion (gms)	0.797	1.066	0.942	0.966	0.836	0.937	1.013	1.066	1.087	0.968	0.865	0.997	1.096
% loss on digestion	9.1	13.0	22.0	9.4	5.6	12.4	13.0	12.3	8.3	18.6	12.4	33.2	5.7
% loss on ignition	13.43	11.63	13.27	-	12.92	17.18	-	11.63	14.26	13.64	12.02	2.19	17.97
Calculated Nb_2O_5 (gms) extracted from 2 grams pyrochlore	.84	.98	.83	-	.81	.86	-	.98	.93	.95	.86	.98	.90

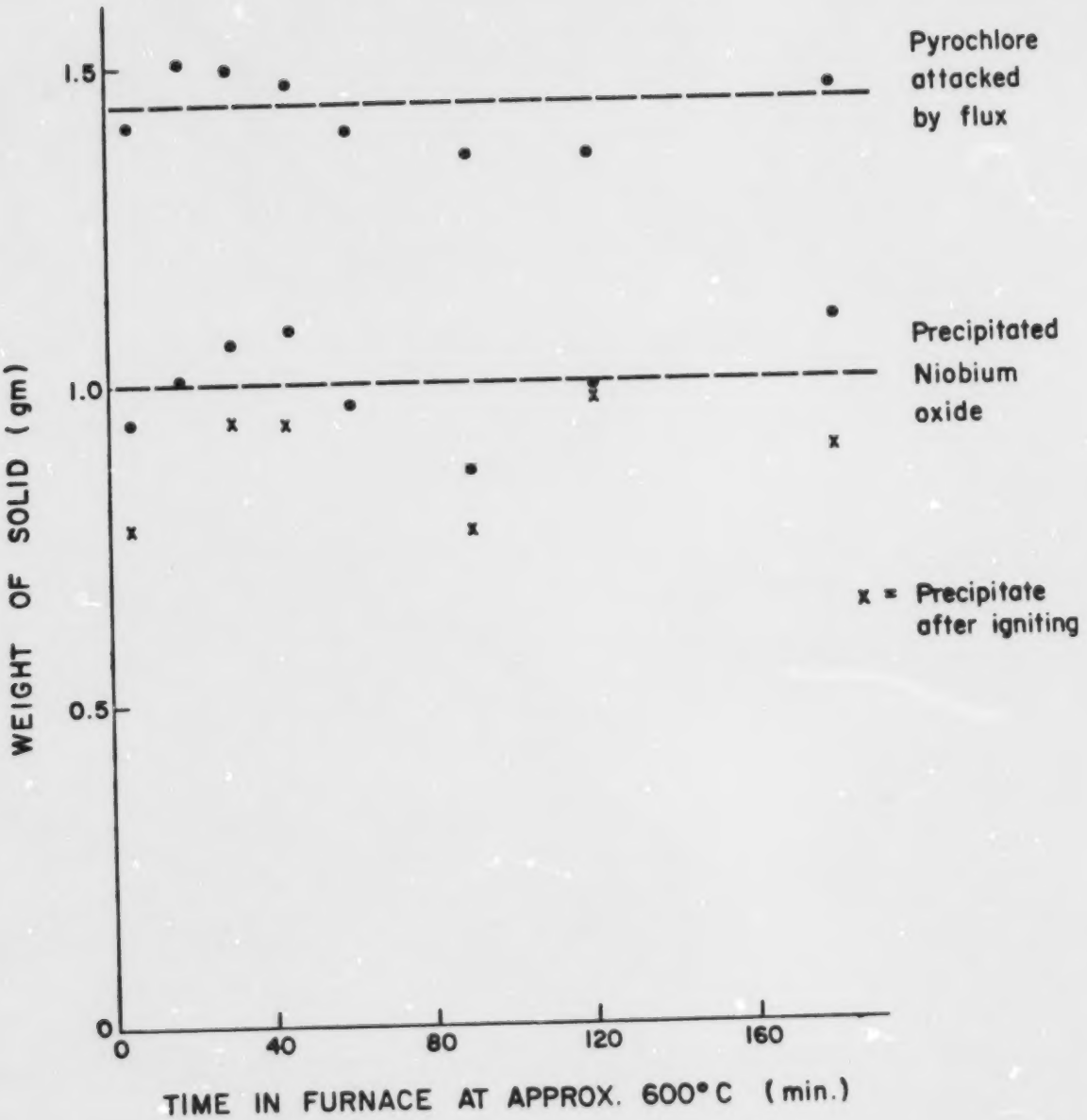


Figure 11
Pyrochlore Solubilized by Flux and Niobium Oxide Precipitated as a Function of Fusion Temperature

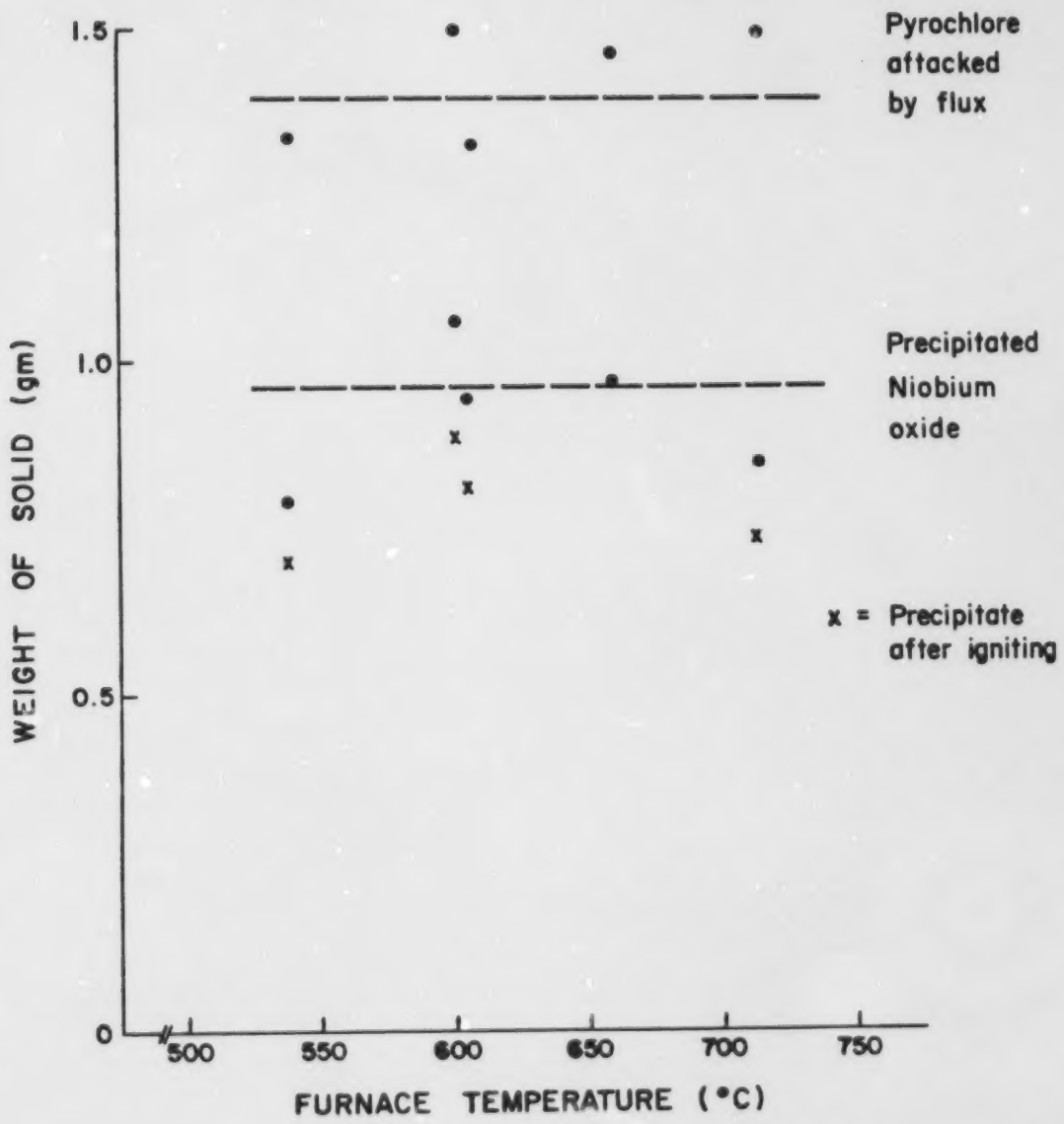


Figure 12
Pyrochlore Solubilized by Flux and Niobium Oxide Precipitated as a Function of Furnace Temperature

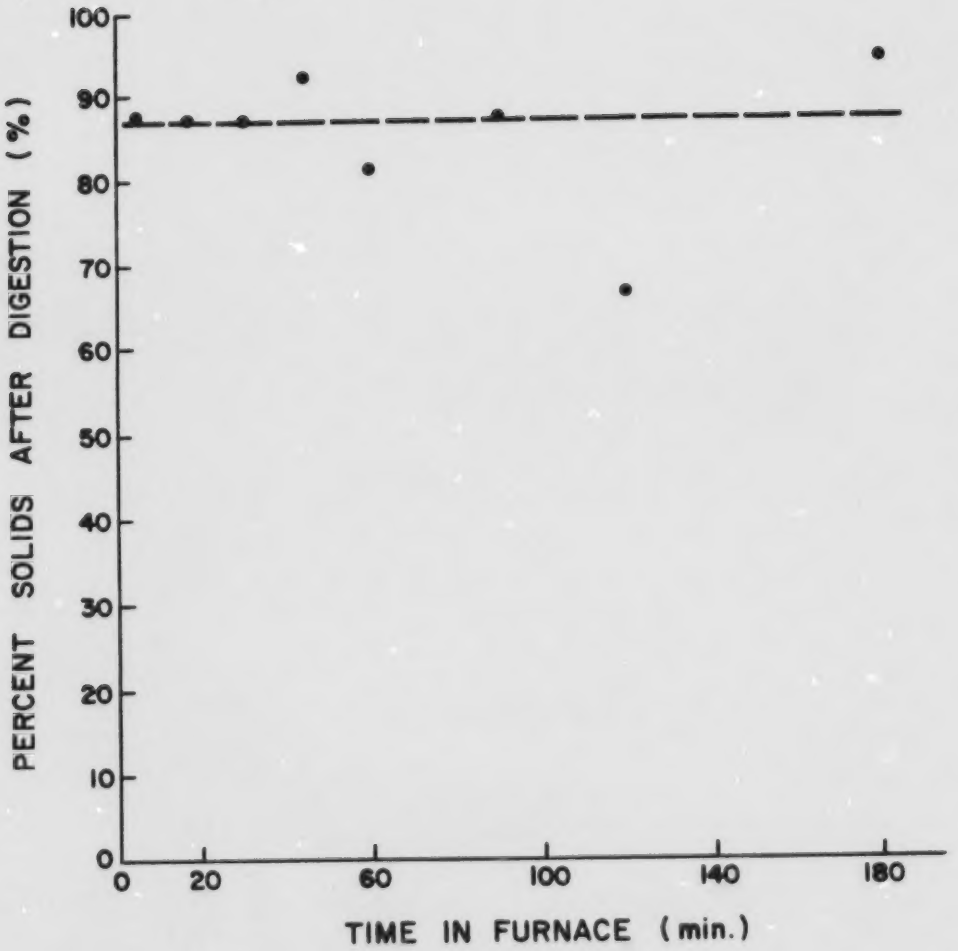


Figure 13
Niobium Oxide Present as a Function of Fusion Time

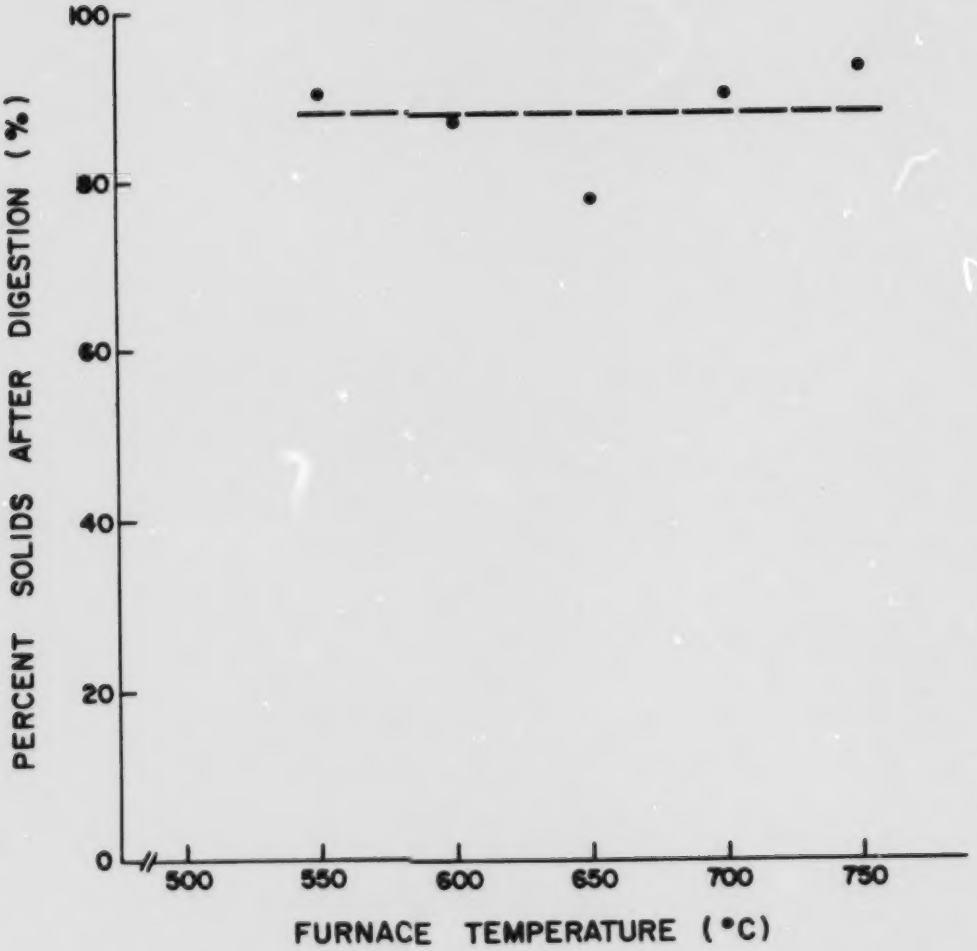


Figure 14
Niobium Oxide Present as a Function of Fusion Temperature

Table 8: **X-RAY FLUORESCENCE ANALYSES**

Chemical Analysis	Pyrochlore Ore		Precipitated Niobium	
	Sample 1	Sample 2	Ignited Sample	Not Ignited Sample
Nb_2O_5	57.3	60.2	90.3	74.5
SiO_2	0.8	0.89	0.52	0.51
Al_2O_3	0.07	0.09	0.10	0.09
CaO	5.86	5.98	0.06	0.11
MgO	0.85	0.88	0.86	0.67
Na_2O	4.77	4.88	1.54	1.29
K_2O	0.15	0.14	0.22	0.37
Fe_2O_3	0.90	0.93	0.05	0.10
MnO	0.10	0.10	0.01	0.01
TiO_2	1.33	1.34	1.34	1.49
P_2O_5	0.11	0.11	0.15	0.16
Cr_2O_3	.01	.01	--	Cr 80 ppm
Ta_2O_5	.02	.03	0.09	Rb 10 ppm
LOI	1.00	1.16	1.00	Sr 510 ppm
F	3.6	3.2	0.89	Zr 960 ppm
				LOI 18.5%

Table 9: **EMISSION SPECTROSCOPY ANALYSES**

Solution I - 250 mg pyrochlore in solution (200 ml)

Nb	570 ppm	= 165 mg Nb_2O_5
Fe	21.7	
Ta	41	
Ca	125	
Ti	24.3	

Solution II - 150 mg pyrochlore in solution (200 ml)

Nb	330 ppm	= 94 mg Nb_2O_5
Fe	13.3	
Ta	27	
Ca	75	
Ti	14.3	

Solution III - 200 mg Nb_2O_5 in solution (200 ml)

Nb	700 ppm	= 200 mg Nb_2O_5

Solution IV - 100 mg Nb_2O_5 in solution (200 ml)

Nb	340 ppm	= 98 mg Nb_2O_5

APPENDIX I

APPENDIX I

Analysis of Flux Following Fusion

Chloride

1.49 gms Cl^- - determined analytically

$\frac{1.49 \text{ gms}}{35.4 \text{ g/mole}}$ = .042 moles Cl^-

therefore: .042 moles NaCl

.042 moles x 58.44 g/mole = 2.45 gms NaCl

2.5 gms NaCl starting material - 2.45 gms = .05 gms NaCl (defined by chloride) lost

$\frac{0.05 \text{ gms}}{58.44 \text{ g/mole}}$ = .00086 moles NaCl lost

therefore: .00086 moles Cl^- - available for gas evolution

Sulfate

1.35 gms sulphate as SO_4^{2-} determined analytically

$\frac{1.35 \text{ gms}}{96.06 \text{ g/mole}}$ = .014 moles SO_4^{2-} present

therefore: .007 moles $K_2S_2O_7$ present

Assuming;

$K_2S_2O_8 \longrightarrow K_2S_2O_7 + \frac{1}{2}O_2$

then, if .007 moles $K_2S_2O_8$ used as starting material,

.007 moles x 270.33 g/mole = 1.90 gms $K_2S_2O_8$ represented

therefore: 2.5 gms starting material - 1.90 gms = 0.60 gms not accounted for

Some weight loss may be lost due to
a. water in original material.
b. trace SO_2, SO_3 gas evolved.
c. oxygen lost to combine with chloride gas

APPENDIX II

Royal Ontario Museum

100 Queen's Park
Toronto, Ontario
Canada M5S 2C6
Cables: ROMA Toronto

ROM

DEPARTMENT OF MINERALOGY & GEOLOGY

416: 978-3647

March 28th, 1984

Ms. Rose Pontarini,
Research & Development,
Scintrex,
222 Snidercroft Road,
Concord, Ontario
L4K 1B5

Dear Ms. Pontarini:

We have completed our x-ray diffraction work on the samples of treated and untreated pyrochlore.

The untreated sample gave an x-ray powder diffraction pattern for the pyrochlore group. Two different kinds of patterns were produced from the treated samples. The orange coloured grains gave a pyrochlore pattern and the white material gave a totally different pattern, which could not be matched with the patterns of any minerals. In view of the treatment which the pyrochlore was subjected to, this product could be almost anything.

Our invoice is enclosed.

Sincerely,

J. A. Mandarino

J. A. Mandarino,
Curator of Mineralogy

JAM/hd
Encl.

APPENDIX III

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

Research and Technology
Recherche et technologie

Canada Centre for Mineral and Energy Technology,
555 Booth Street
Ottawa, Ontario
K1A 0G1

Centre canadien de la technologie des minéraux et de l'énergie,
555, rue Booth,
Ottawa (Ontario)
K1A 0G1

MINERAL SCIENCES LABORATORIES
EXTRACTIVE METALLURGY LABORATORY

Your file Votre référence

Our file Notre référence

January 13, 1984

Mrs. Rose Pontarini
Scintrex Ltd.
222 Snidercroft Road
Concord, Ontario
L4K 1B5

Dear Mrs. Pontarini:

Enclosed is a copy of the report on the scanning electron microscope examination of Sample No. 3 "3000 mg pyrochlore fused with 10 g flux (20% chloride/80% persulphate) and dissolved in 2M HCl, then digested. 19.09.83". Since oxygen is not detected by the energy dispersive X-ray analysis (EDXA) the elements reported can be present as oxides, hydroxides or oxyanions.

The X-ray diffraction results, which I had summarized to you by phone, were as follows:

Sample No. 1. "1000 mg pyrochlore mixed with 200 mg Nb_2O_5 (pure). 20.09.83"

Phases detected: pyrochlore; Nb_2O_5; trace hematite; possible trace unidentified phase.

Hand-picked material separated from the mixture:

a. White material: Nb_2O_5
b. Black particles: hematite; pyrochlore
c. Glassy-like material: pyrochlore

Sample No. 4. "Pyrochlore only"

Phases detected: pyrochlore

Sample No. 3. as described above

Phases detected: pyrochlore; halite; rutile (minor amount)

Hand-picked material separated for examination:

a. Black particles: rutile.
b. White to yellowish material: halite; trace unidentified.

Canada

.../2

The X-ray diffraction can only detect crystalline phases; any amorphous material would not give an X-ray diffraction pattern. Even so, there is some difficulty in reconciling the results of the two methods of examination; there may possibly be differences due to sampling as only very small amounts of material are taken for each examination. The hematite (Fe_2O_3) and rutile (TiO_2) reported by X-ray diffraction probably arose from impurities in the pyrochlore. It is clear from the EDXA analyses that niobium occurs in the leach residue along with other constituents of the charge. However, it would not be possible to make any quantitative estimation of the amount of non-pyrochlore niobium in the residue by these techniques.

Thank you for your November progress report, which arrived a few weeks ago.

With best wishes for the New Year,

Yours sincerely,

Hugh Webster

A.H. Webster
Physical Chemistry Section

AHW:lp
Encl.

MINERAL PROCESSING LABORATORY

MINERALOGY SECTION

Report M - 3385

TITLE: Scanning electron and qualitative energy dispersive analysis on a niobium-rich leach residue.

PROJECT NO.: 3.3.0.2.06 "Non-Ferrous Pyrometallurgical Slags".

SAMPLE: A sample of a niobium-rich residue resulting from a HCL leach of a powdered pyrochlore fused with NaCl-$K_2S_2O_8$ flux was received from Dr. H. Webster, Physical Chemistry Section, EML, in November 1983. Dr. Webster stated that the leach residue had originally been submitted to CANMET by a contractor working on "Low Temperature Fluxes in Metallurgy" (CANMET contract 03SQ23440-3-9062).

PURPOSE: To identify the phases present in the leach residue and to assess their composition qualitatively using energy dispersive analysis (EDXA). Powder-X-ray diffraction analysis have indicated residual NaCl and pyrochlore. Another niobium oxide phase is suspected; its abundance and composition is required.

METHOD OF INVESTIGATION: A single polished section was prepared from the leach residue using a water-free environment, in order to prevent dissolution of any salts that might be present. As is often the case when this type of polishing procedure is used, most of the phases in the leach residue did not polish well enough to be discriminated microscopically. Therefore, the identification and characterization of these phases was made using the back-scattered electron and EDXA modes of the SEM.

RESULTS: The examination of the leach residue showed that it is composed essentially of various sized agglomerates (Figure 1), the majority of which consist of very fine-grained particles (Figure 2). A smaller number exhibit a coarser particle size (Figure 3). Syneresis cracks are prevalent in the fine-grained agglomerates (Figures 1 and 2). The balance of the leach residue is composed of small amounts of partly reacted pyrochlore and trace amounts of silicate.

Qualitative EDXA analyses were made on many of the fine-grained agglomerates. The composition varies somewhat from spot to spot but basically consists of niobium, potassium and sulphur with minor to trace amounts of titanium and chlorine. Calcium, iron, aluminum and silicon occur in random and trace amounts. Similar studies on the coarser particles in some agglomerates (Figure 3) showed that they are composed largely of potassium, calcium and sulphur (possibly a sulphate?) with minor niobium. These larger particles may be multi-phase but this could not be ascertained positively. The matrix is similar to that of the fine-grained agglomerates mentioned above. No discrete sodium chloride or other salt was detected.

The partly reacted pyrochlore grains (Figure 4) consist of a core of calcium, sodium niobate plus minor titanium rimmed by a continuous layer containing equivalent niobium but also appreciable potassium, minor titanium and trace amounts of iron, calcium and manganese.

The only silicate found in the leach residue was a potassium alumino-silicate. It occurs in trace amounts.

Approved _____ Signed D. Owens Date Jan. 4/84

Section Head Mineralogy Section

Copies to: 1. Dr. H. Webster 2. D. Owens 3. _____

4. M.P.L. Files 5. Section Files

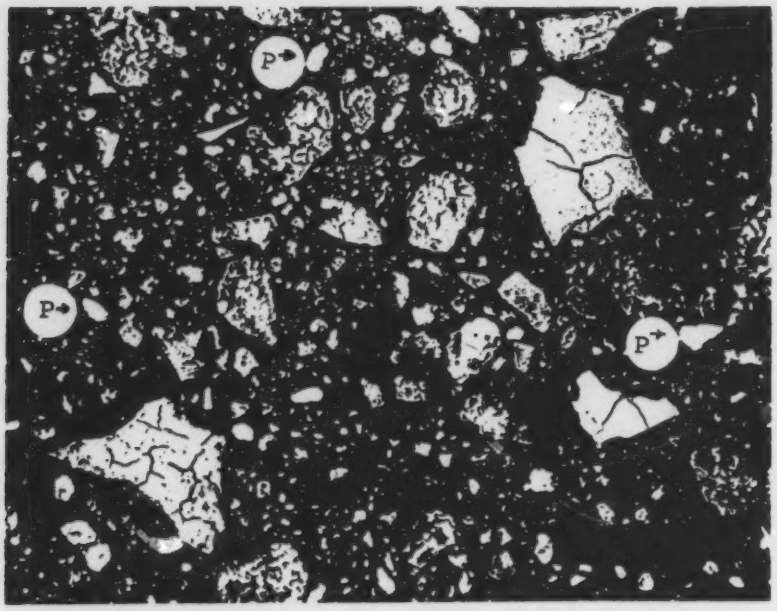


Figure 1. Back-scattered electron micrograph of the polished section prepared from the leach residue showing that it is composed essentially of various sizes of agglomerates (shades of grey with cracks) and that only a very small amount of pyrochlore (P) is present. The black background represents the mounting medium.

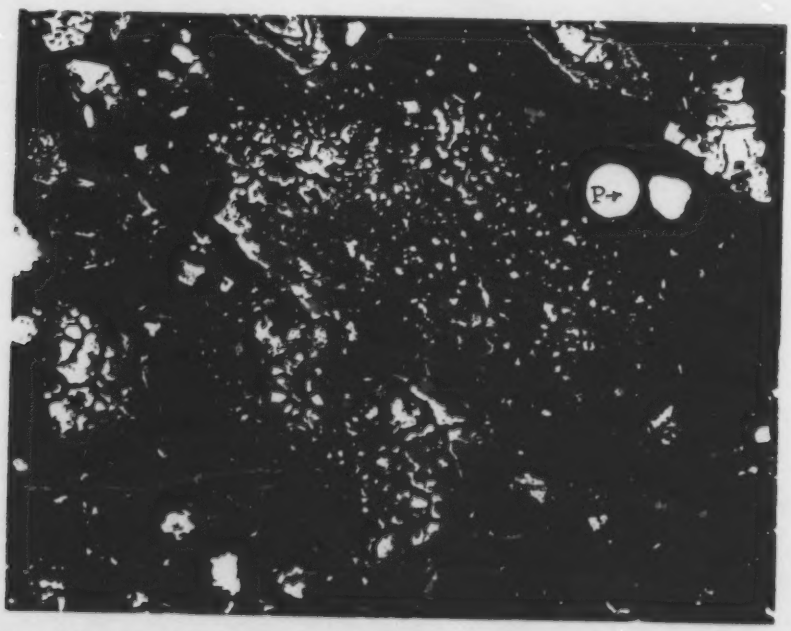


Figure 2. Back-scattered electron micrograph of the polished section prepared from the leach residue showing several typical agglomerates at higher magnification. Several pyrochlore grains are also shown (P). The black background is mounting medium.

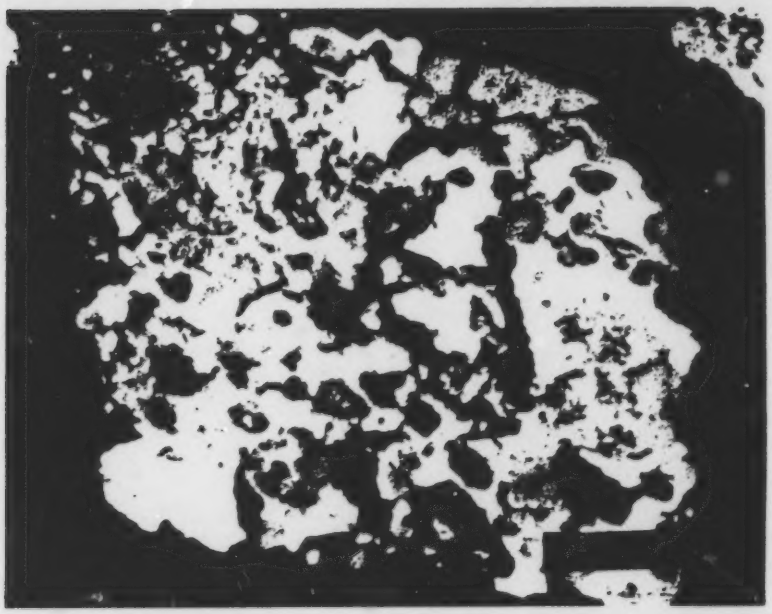


Figure 3. Backscattered electron micrograph of the polished section prepared from the leach residue showing an agglomerate with larger discrete particles (medium to light grey) in a fine-grained matrix (white).EDXA shows the darker grains are composed of Ca,K and S with minor Nb (sulphate?). The matrix is basically Nb, K and S with minor Ti. It is believed that the darker areas may be multi-phase.

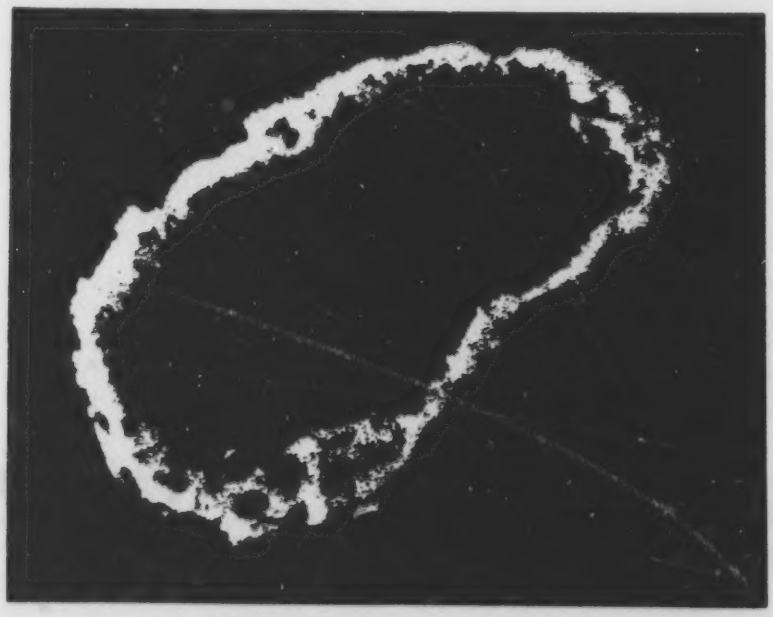
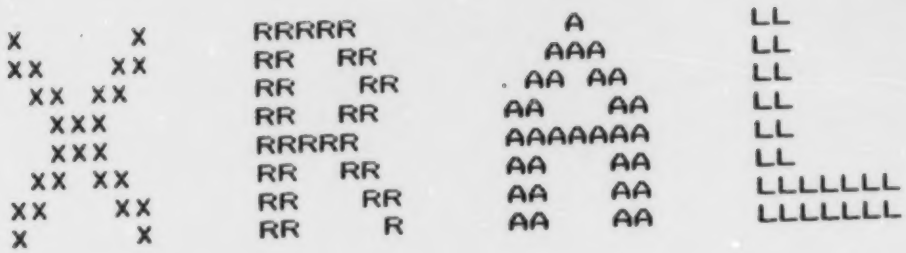


Figure 4. Back-scattered electron micrograph of the polished section prepared from the leach residue showing a grain of pyrochlore (medium grey) rimmed by an alteration product (greyish white).

APPENDIX IV



XRF - WHOLE ROCK ANALYSIS

SCINTREX LIMITED
Attn: J. KINRADE
222 SNIDERCROFT ROAD
CONCORD, ONTARIO
L4K 1B5

CUSTOMER No. 739

DATE SUBMITTED
3-JAN-84

REPORT 20130 REF. FILE 15777 DATE REPORTED 24-JAN-84

XRF W. R. A. SUMS INCLUDE ALL ELEMENTS DETERMINED.
FOR SUMMATION ELEMENTS ARE CALCULATED AS OXIDES.

NOTE: FOR DUPLICATE DETERMINATIONS BY DIFFERENT METHODS, VALUES APPEAR IN ORDER OF LISTING ON HEADER PAGE.

X-RAY ASSAY LABORATORIES LIMITED

1885 LESLIE STREET, DON MILLS, ONTARIO M3B 3J4

PHONE 416-445-5755 TELEX 06-986947

CERTIFICATE OF ANALYSIS

TO: SCINTREX LIMITED
ATTN: J. KINRADE
222 SNIDERCROFT ROAD
CONCORD, ONTARIO
L4K 1B5

CUSTOMER NO. 739

DATE SUBMITTED
3-JAN-84

REPORT 20130

REF. FILE 15777-P4

2 PULPS P.O. 30692

WERE ANALYSED AS FOLLOWS:

	METHOD	DETECTION LIMIT
WRMAJ %	WR	0.010
WRMIN PPM	WR	10.000
MN PPM	DCP	2.000
FE PPM	DCP	2.000
NI PPM	DCP	1.000
NB2O5 %	XRF	0.010
PB PPM	DCP	2.000
PB %	XRF	0.010

X-RAY ASSAY LABORATORIES LIMITED

CERTIFIED BY .....

DATE 24-JAN-84

*** UNLESS INSTRUCTED OTHERWISE WE WILL DISCARD PULPS 180 DAYS ***
AND REJECTS 90 DAYS FROM DATE OF THIS REPORT

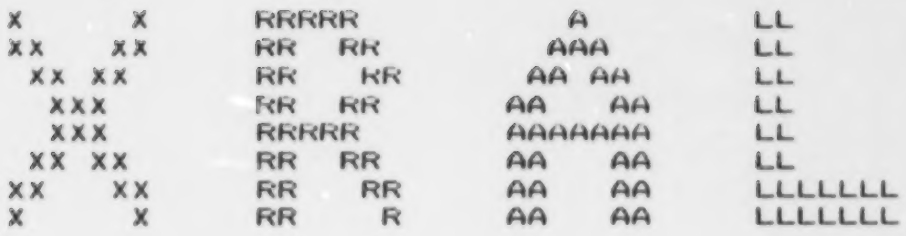
X-RAY ASSAY LABORATORIES 24-JAN-84 REPORT 20130 REFERENCE FILE 15777 PAGE 1

SAMPLE	SIO2	AL203	CAO	MGO	NA20	K20	FE203	MNO	TI02	P205	LOI	SUM
NB022-83	0.51	0.09	0.11	0.67	1.29	0.37	0.10	0.01	1.49	0.16	18.5	23.5

SAMPLE	CR	RB	SR	ZR
NB022-83	80	<10	510	960

SAMPLE	MN PPM	FE PPM	NI PPM	NB2C5 %	PB PPM	PB %
N8022-83	--	--	--	74.5	--	--
NSW-1	23	740	3	--	>4CCC	1.58

> - CONCENTRATION TOO HIGH FOR TREATMENT BY GECCHEMICAL METHCD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XX XX RR RR AAA LL
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XXX RR RR AA AA LL
XXX RRRRR AAAAAAA LL
XX XX RR RR AA AA LL
XX XX RR RR AA AA LLLLLLL
X X RR R AA AA LLLLLLL

XRF - WHOLE ROCK ANALYSIS

SCINTREX LIMITED
Attn. ROSE PONTARINI
222 SNIDERCROFT ROAD
CONCORD, ONTARIO
L4K 1B5

CUSTOMER No. 739

DATE SUBMITTED
1-FEB-84

REPORT 20373 REF. FILE 15967 DATE REPORTED 27-FEB-84

XRF W. R. A. SUMS INCLUDE ALL ELEMENTS DETERMINED.
FOR SUMMATION ELEMENTS ARE CALCULATED AS OXIDES.

NOTE: DUE TO THE SPECIAL MATRIX, THESE SAMPLES LIE OUTSIDE OF THE WHOLE ROCK ANALYSIS LIMITS.

REPORTED VALUES CANNOT BE GUARANTEED ACCURATE.

X-RAY ASSAY LABORATORIES LIMITED

1885 LESLIE STREET, DON MILLS, ONTARIO M3B 3J4

PHONE 416-445-5755 TELEX 06-986947

CERTIFICATE OF ANALYSIS

TO: SCINTREX LIMITED
ATTN: ROSE PONTARINI
222 SNIDERCROFT ROAD
CONCORD, ONTARIO
L4K 1B5

CUSTOMER NO. 739

DATE SUBMITTED
1-FEB-84

REPORT 20373

REF. FILE 15967-84

2 SAND,1 PULP P.O. 31349

WERE ANALYSED AS FOLLOWS:

	METHOD	DETECTION LIMIT
F %	WET	0.010
WRMAJ %	XRF	0.010
WRMIN PPM	XRF	10.000
NB2O5 %	XRF	0.010
TA2O5 %	XRF	0.010

X-RAY ASSAY LABORATORIES LIMITED

DATE 27-FEB-84

CERTIFIED BY .....

*** UNLESS INSTRUCTED OTHERWISE WE WILL DISCARD PULPS 180 DAYS ***
AND REJECTS 90 DAYS FROM DATE OF THIS REPORT

X-RAY ASSAY LABORATORIES 27-FEB-84 REPORT 20373 REFERENCE FILE 15967 PAGE 1

SAMPLE	SIO2	AL2O3	CAO	MGO	NA2O	K2O	FE2O3	MNO	TIO2	P2O5	CR2O3	LOI	SUM
A1	0.80	0.07	5.86	0.85	4.77	0.15	0.90	0.10	1.33	0.11	<0.01	1.00	17.3
A2	0.89	0.09	5.98	0.88	4.88	0.14	0.93	0.10	1.34	0.11	<0.01	1.16	17.8
B3	0.52	0.10	0.06	0.86	1.54	0.22	0.05	0.01	1.34	0.15	---	1.00	5.99

SAMPLE	CR	RB	SR	ZR
A1	---	<10	8210	2540
A2	---	<10	8330	2560
B3	70	<10	50	860

SAMPLE	F %	NB2O5 %	TA2O5 %
A1	3.60	57.3	0.02
A2	3.20	60.2	0.03
B3	0.89	90.3	0.09

X-RAY ASSAY LABORATORIES LIMITED

1885 LESLIE STREET, DON MILLS, ONTARIO M3B 3J4

PHONE 416-445-5755 TELEX 06-986947

CERTIFICATE OF ANALYSIS

TO: SCINTREX LIMITED
ATTN: ROSE PONTARINI
222 SNIDERCROFT ROAD
CONCORD, ONTARIO
L4K 1B5

CUSTOMER NO. 739

DATE SUBMITTED
3-FEB-84

REPORT 20292

REF. FILE 15976-A3

4 SOLUTIONS P.O. #31349

WERE ANALYSED AS FOLLOWS:

	METHOD	DETECTION LIMIT
FE PPM	DCP	0.100
NB PPM	DCP	10.000
TA PPM	DCP	1.000
CA PPM	DCP	1.000
TI PPM	DCP	0.100

X-RAY ASSAY LABORATORIES LIMITED

CERTIFIED BY .....

DATE 10-FEB-84

*** UNLESS INSTRUCTED OTHERWISE WE WILL DISCARD PULPS 180 DAYS ***
AND REJECTS 90 DAYS FROM DATE OF THIS REPORT

SAMPLE	FE PPM	NB PPM	TA PPM	CA PPM	TI PPM
SOLUTION # IB	21.7	570	41	125	24.3
SOLUTION # IIB	13.3	330	27	75	14.3
SOLUTION # IIIB	--	700	--	--	--
SOLUTION # IVB	--	340	--	--	--

APPENDIX V

SAMPLE SOLUTIONS

Solution IB - 250 mg pyrochlore in solution (200 ml)

570 ppm Nb

570 μg/ml x 200 ml = .114 gms Nb

$\frac{.114}{92.906}$ gms Nb = .0012 moles Nb

.0012 moles Nb → .0006 moles Nb_2O_5

.0006 moles x 265.81
= .165 gms compared to .145 gms Nb_2O_5 actually present (assuming 58% Nb_2O_5 in pyrochlore).

Solution IIB - 150 mg pyrochlore in solution (200 ml)

330 μg/ml = 66000 g Nb = .066 g

$\frac{.066}{92.906}$ g/mole = .0007 moles Nb

.0007 moles Nb → .000355 moles Nb_2O_5

.000355 moles x 265.81 = .094 gms Nb_2O_5 compared to .087 gms actually present (assuming 58% Nb_2O_5 in pyrochlore).

STANDARD SOLUTIONS

Solution IIIB - 200 mg Nb_2O_5 in solution (200 ml)

700 ppm Nb

700 $\frac{\mu g}{ml}$ x 200 ml = .14 gms

$\frac{.14}{92.906}$ g/mole g Nb = .0015 moles Nb

therefore - .00075 moles Nb_2O_5

.00075 moles x 265.81 g/mole = $\frac{200}{}$ mg Nb_2O_5

which is exactly what was used.

Solution IVB - 100 mg Nb_2O_5 in solution (200 ml)

340 ppm Nb

This is almost one-half of the above and therefore compares equally well to the amount of niobium oxide used.

APPENDIX VI

HATCH ASSOCIATES LTD.

P.R. #8824.1
File #8824.1

February 9, 1984

PROJECT REPORT

Distribution:

J. Kinrade (3) ✓

E.H. Nenniger
A.G.W. Lamont

SCINTREX FLUXING PROGRAM - 8824

DISPOSAL OF THE SPENT SOLUTIONS

Contents

1.0 SUMMARY

2.0 THE REACTIONS

3.0 SOLUBILIZATION OF PYROCHLORE

4.0 THE LEACH SOLUTION

5.0 THE RECYCLE OF POTASSIUM

6.0 THE MAKEUP OF SULPHATE & HYDROGEN

7.0 DISPOSAL OF LEACH SOLUTIONS AS WASTE

8.0 COMPARISON OF COSTS

This note deals with an estimation of some of the technical and economic aspects of disposing of spent solution from the Scintrex fusion process. All of the development here has been done in relation to pyrochlore.

1.0 SUMMARY

1.1 It is expected that most of the potassium entering the fusion step (as potassium persulphate) will appear in the aqueous leach solution as the sulphate and the bisulphate.

1.2 Potassium sulphates could be recovered from waste solution by evaporation and crystallization. The "classical" process for manufacture of potassium peroxydisulphate involves double decomposition of potassium bisulphate and ammonium peroxydisulphate, the resulting ammonium bisulphate being then reconverted by electrolysis.

1.3 If potassium were recovered and recycled, the fundamental losses from the system would be sulphate associated with waste metal sulphates, and hydrogen from the electrolytic cells. The fundamental chemical makeup in this case would be sulphuric acid.

1.4 If potassium were not to be recovered and recycled, waste disposal regulations would require neutralization of the acid content and removal of most of the iron. These could be arranged by addition of lime. We expect that the resulting solid residue or mud would be high in potassium sulphate; the remaining solution would also still contain substantial amounts of potassium sulphate. The former would and the latter might present a problem for disposal as waste. However, it is possible that both mud and solution could be sold for their fertilizer value.

1.0 SUMMARY (Cont'd)

1.5 In the case of pyrochlore, a comparison of the most important of the costs associated with disposal and with recycle shows that recycling is far preferable economically.

1.6 The cost of chemicals for the Scintrex fusion process applied to pyrochlore, when recycling potassium and including the cost of doing so, is estimated at roughly \$6.00 /kg Nb_2O_5.

2.0 THE REACTIONS

The fusion of a mineral with persulphate results, among other things, in the sulphation of some metal oxides. In relation to the eventual aqueous "waste", this is probably the most significant process; the reaction is, in essence:

$$K_2S_2O_8 + MO = K_2SO_4 + MSO_4 + \tfrac{1}{2} O_2$$

It will be noted that of two atoms of sulphur in the flux, one is effective in sulphating the MO and the other must remain with the potassium sulphate formed.

Excess persulphate in fusion will loose oxygen:

$$K_2S_2O_8 = K_2S_2O_7 + \tfrac{1}{2} O_2$$

The pyrosulphate so formed, when it comes to the leaching step, will immediately hydrolyze:

$$K_2S_2O_7 + H_2O = 2KHSO_4$$

The aqueous solution from the leach step will, therefore, contain K_2SO_4, $KHSO_4$, and M sulphates as its primary components. Sodium chloride will also be present to the extent it is present in the flux mix. The amounts of these various compounds to be dealt with can be calculated closely enough for present purposes.

2.0 THE REACTIONS (Cont'd)

Scintrex reported (in its October Report) that the loss of chlorine in fusion amounted to only 2% and of sulphur less than 18%; these are low enough to be ignored at present.

3.0 SOLUBILIZATION OF PYROCHLORE

The analysis of the pyrochlore being used at Scintrex is not known; however, it originated with SOQUEM, and is thought to be close in analysis to the numbers given in Table I.

Fluoride is probably not solubilized, and probably removes some of the calcium as CaF_2. If this is so, then the calculated persulphate consumption will be too high. Niobium is shown as not accounting for persulphate and not forming M sulphate; whether this is so or not is unimportant, as the leaching step will hydrolyze it, if formed in fusion, to make sulphuric acid, and the overall net effect is the same as if it had not formed! The significance of fluoride in relation to niobium has not been assessed.

The total consumption of persulphate in sulphating M oxides, added up from Table 1, is 157 gm/100 gm pyrochlore. The amount of K_2SO_4 simultaneously formed is 101 gm/100 gm pyrochlore plus 6 gm from potassium in the pyrochlore.

4.0 THE LEACH SOLUTION

The total flux consumption is given by Scintrex as $\frac{100}{0.27}$, or 370 gm/100 gm pyrochlore, and the composition as 10-20% Na Cl. Using 10% Na Cl, the consumption of common salt is 37 gm and of potassium persulphate 333 gm, per 100 gm of pyrochlore. Of the persulphate, 157 gm is used in sulphation of the MO, leaving 176 gm to form pyrosulphate in fusion and bisulphate in leaching. The amount of bisulphate so formed would be 166 gm. The amounts of various compounds to be dissolved out of the flux mass will be as shown in Table 2.

TABLE 1

PYROCHLORE COMPOSITION AND SOLUBILIZATION

Item	Analysis %	Sulphated	Solubilized	Amount, gm/100 gm pyrochlore $K_2S_2O_8$ Consumed	M Sulphate Formed
Nb_2O_5	60	No	No	0	0
Ta_2O_5	0.2	No	No	0	0
Al_2O_3	0.2	No	No	0	0
SiO_2	1.5	No	No	0	0
ZrO_2	1	No	No	0	0
Fe	5	Yes	Yes	36	18
Na_2O	5	Yes	Yes	22	11
CaO	15	Yes	Partial	72	36
K_2O	3	Yes	Yes	9	6
TiO_2	4	Yes	Yes	27	12
F	5	-	?	0	0

TABLE 2

COMPOUNDS TO BE DISSOLVED IN LEACHING

Item	Amount to be Dissolved gm/100 gm Pyrochlore	Approximate Solubility at 100°C, Single Component, gm/l Solution
Na Cl	37	350
K_2SO_4	107	220
$KHSO_4$	166	1000
$Fe_2(SO_4)_3$	18	See Note
$Na_2 SO_4$	11	400
$Ti(SO_4)_2$	12	See Note
$Ca SO_4$	36	1.5

Note:

Iron and titanium will hydrolyze (decompose) from their sulphate solutions at 100°C in some conditions. The significance of this fact, and how to deal with it, we propose to leave to experimental work, proceeding here as if they dissolved without complication.

4.0 THE LEACH SOLUTION (Cont'd)

We judge from Table 2 that the volume of leach solution needed may be dictated primarily by the amount of potassium sulphate to be dissolved, depending upon the route to be followed in treatment of the eventual waste solution. If the solutions are to be recycled, then the volume could be minimized by adding sulphuric acid, sufficient to convert the potassium sulphate to bisulphate - a step necessary in any case eventually in the recycle process. If, however, the solution is, in fact, to be wasted, then sulphuric acid so added would also enter the waste stream, adding to the waste load to no advantage.

If no sulphuric acid is added, the amount of potassium sulphate to be dissolved indicates a minimun single-contact solution volume of about 500 ml/100 gm pyrochlore; in practice this would probably become about 800 ml/100 gm. The Nb_2O_5 content (as a fine suspension) would amount to about 80 gpl. If sulphuric acid were added, the total amount of $KHSO_4$ to be dissolved would be about 340 gm/100 gm pyrochlore. The solution volume might in this case be kept down to 400 - 500 ml/100 gm pyrochlore. The estimated analysis of the solution is given in Table 3.

5.0 THE RECYCLE OF POTASSIUM

Potassium enters the fusion process as crystalline dry potassium peroxydisulphate. This material was made in large amounts in Germany during the war using a process that is still the principal commercial route to the best of our knowledge. The only published descriptions with great detail are those on the wartime German experience (see Chem. Eng., Aug. 1948).

Potassium persulphate is the product of the electrolysis of potassium bisulphate - but the direct route is not useful industrially because of the low solubility of the persulphate in water (about 20 gpl). In the commercial process, the much more soluble ammonium bisulphate is electrolyzed to the persulphate, the strong solution of the latter then being subjected to double decomposition with

TABLE 3

THE SOLUTION TO BE DEALT WITH

Item	Content in gm/h: In event of disposal to Waste	In event of disposal to Reuse	Solubility at 10°C (approx.) gpl
Na Cl	45	75	300
K_2SO_4	135	--	90
$KHSO_4$	208	680	400
$Fe_2(SO_4)_3$	22	35	--
$Na_2 SO_4$	15	25	250
$Ti(SO_4)_2$	15	25	--
$Ca SO_4$	1.5	1.5	2
Volume - ml/100 gm pyrochlore	800	500	

5.0 THE RECYCLE OF POTASSIUM (Cont'd)

solid potassium bisulphate. Potassium persulphate forthwith precipitates and the ammonium bisulphate solution is reconstituted for electrolysis again.

In our case, the potassium to be recycled must be reclaimed as a relatively dry (centrifuged crystals?) potassium bisulphate or sulphate (to which sulphuric acid could be added). The reclaimed potassium salts would need to be free of some large fraction (say 80%) of the non-potassium salts or impurities in the originating solution. One way of attaining these objectives would be to evaporate water from the solution and crystallize the potassium salts. Because of the high solubility of potassium bisulphate in cold solution, there will tend to be large losses to the mother liquor. However, potassium makeup to the system could perhaps be added as KOH to the mother liquor - the much less soluble potassium sulphate would then be dropped out in large amounts.

Approximately, the amount of water to be evaporated would be 3½ tonnes/tonne pyrochlore. The cost of energy, using triple effect evaporation, would exceed $25/tonne, or $0.02/lb. niobium oxide. If multiple effect evaporation is not possible (because of a scaling effect associated with the calcium content, for example) then substantially higher costs would be incurred.

The process for conversion of potassium bisulphate to the persulphate is outlined in Figure 1. We have not estimated costs for electrolysis and conversion steps in the process. It is our judgment that the cost would total around 2/3 of the price of purchased potassium persulphate, after subtraction of the value of potassium bisulphate contained.

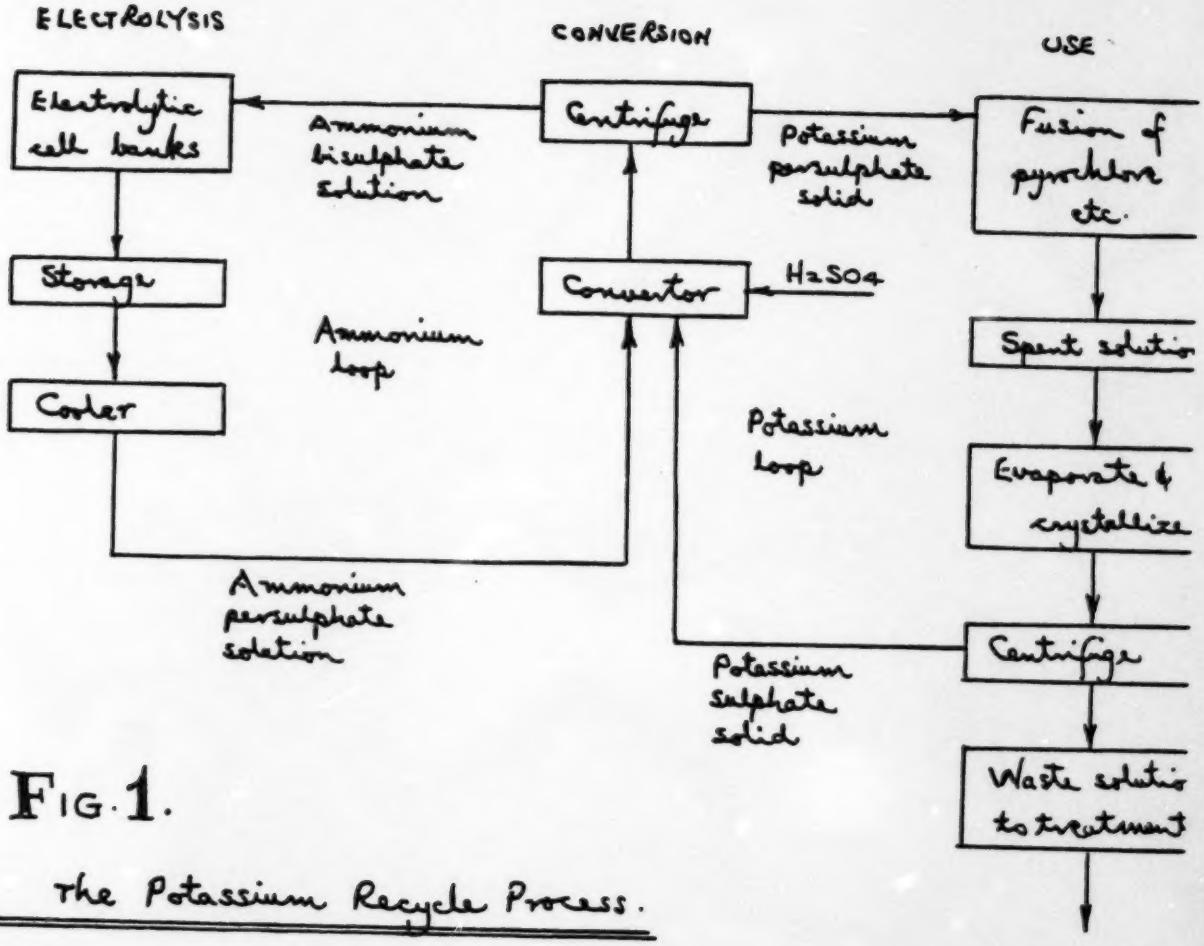

FIG. 1.

The Potassium Recycle Process.

6.0 THE MAKEUP OF SULPHATE AND HYDROGEN

In the overall process, when potassium is recycled, there are two fundamental chemical losses to be made up. One is sulphate; as already discussed, tramp elements are removed and discarded as sulphates. The other chemical loss is hydrogen, from the electrolytic cells. Makeup is needed, therefore, primarily as sulphuric acid. The amount of acid needed can be calculated from Table 3, and is 0.6 tonne/tonne pyrochlore. The cost of this makeup acid would be $25 - $40/tonne pyrochlore.

7.0 DISPOSAL OF LEACH SOLUTIONS AS WASTE

The solution to be disposed of, described in Table 3, is very high in potassium sulphates. It is also substantially acidic and is high in iron content. Existing regulations in most jurisdictions would require that the acid be neutralized and the iron removed. This could be done by addition of lime, followed by thickening. The effect of doing this would be to convert all the potassium to the neutral sulphate, so reducing its solubility, and roughly 2/3 of the potassium sulphate would report in the gypsum mud! Such a mud could not be disposed of to a land fill - but could perhaps be sold for fertilizer. The amount of potassium sulphate contained would be around 1.4 tonne/tonne pyrochlore, with a value possibly as high as $200 /tonne (arbitrarily 75% of that of commercial PS).

For the remaining solution, of composition estimated in Table 4, disposal is governed at present by the total dissolved solids content and its effect on receiving waters. In general, there are no regulations on discharge of potassium, but we think that such regulations would probably come into being in face of a discharge of the kind described in Table 4. Discharge as waste is problematic as we see it.

Again, however, sale as fertilizer might be possible. Putting a value on it at 1/3 that of commercial PS, the solution would have a sales value of $90/tonne PS contained.

TABLE 4

FINAL EFFLUENT FOR DISPOSAL

Item	Content - gpl
Na Cl	45
K_2SO_4	90
Na_2SO_4	15
$CaSO_4$	2

7.0 DISPOSAL OF LEACH SOLUTIONS AS WASTE (Cont'd)

Overall, then, "disposal as waste" could be looked on as sale at distress prices, bringing in a total of about $340/tonne pyrochlore.

8.0 COMPARISON OF COSTS

An outline of part of the costs of the Scintrex fusion process is set forth in Table 5. The costs included are only those that affect the choice between wasting potassium and recycling it, and of those costs only the ones that are thought to be the major ones. (It should be noticed that capital charges are not included, except in the Electrolysis and Conversion aspect of recycling. There, the costing basis used is tantamount to inclusion of capital charges, and properly so).

It is immediately obvious in Table 5 that:

- the sale of potassium sulphate does little in the way of cost reduction
- the recycling of potassium, or the "home" manufacture, of persulphate should be worthwhile
- the cost of potassium persulphate is the overwhelming part of costs. Nothing else contributes much in comparison.

TABLE 5

THE COSTS (PARTIAL) OF EFFLUENT TREATMENT

Chemicals	Unit	Unit Price Can $	Waste Potassium p/t pyrochlore Units	$	Recycle Potassium p/t pyrochlore Units	$
Pot. persulphate	kg	1.75	3300	5750	330	575
Lime	Tonne	50.00	0.5	25	--	--
Sulphuric acid	Tonne	70.00	--	--	0.6	40
Heat	--	--	--	--	--	25
Electrolysis & Conversion	kg KPS	1.00	--	--	2970	2970
Total				$5775		$3610
Sale of pot. sulphate						
- in mud	kg	0.20	1400	280	--	--
- in solution	kg	0.09	700	60	0.1	70
Net				$5435		$3540

Note:

In the recycle route, we have allowed arbitrarily for a 10% loss of potassium, replaced as purchased KPS.